Supporting Information for

Total Synthesis of Phorboxazole A via de novo Oxazole Formation: Convergent Total Synthesis

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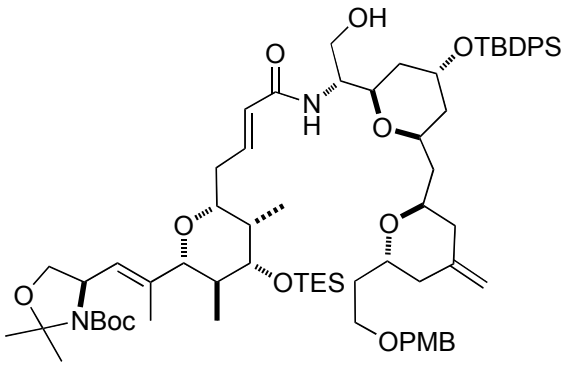
General Methods

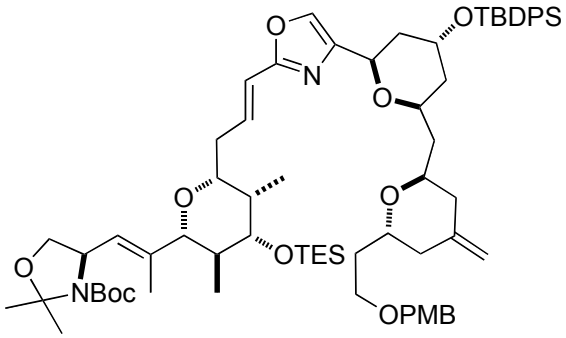
All air and moisture sensitive reactions were carried out under argon in oven-dried glassware using standard syringe, cannula and septa techniques. Unless otherwise noted, all reactions were carried out at room temperature (20-25 °C). Molecular sieves were activated by heating at 120 °C for 24 hours. Tetrahydrofuran (THF), methylene chloride (CH_2Cl_2), diethyl ether (diethyl ether), toluene and dimethylformamide (DMF) were either purified using a Pure Solv solvent purification system or by the following methods: THF and diethyl ether were distilled from Na/benzylphenone ketyl under nitrogen. CH_2Cl_2, toluene, benzene, acetonitrile (CH_3CN), triethylamine (Et_3N), *N*,*N*-diisopropylethylamine (*i*-Pr_2NEt), hexanes, and *n*-pentane were distilled from CaH_2 under nitrogen. Dimethylsulfoxide (DMSO) and DMF were dried over activated 4 Å molecular sieves. Methanol was dried over activated 3 Å molecular sieves. Trifluoroacetic acid (TFA) was distilled under argon. Deuterated chloroform ($CDCl_3$) was neutralized with anhydrous potassium carbonate. Other reagents were used as received from commercial sources unless otherwise noted. Flash column chromatography was performed using Baker Flash silica gel 60 or Silicylce Silicaflash P60 silica gel. Analytical TLC was performed with 25 μm Merck Kieselgel (EM Science) silica gel 60 F_{254} plates, visualized by fluorescence upon 254 nm irradiation and/or staining with anisaldehyde reagent (450 mL of 90% ethanol, 25 mL of sulfuric acid, 15 mL of acetic acid, and 25 mL of anisaldehyde). The solvent combinations for flash column chromatography, TLC, and recystalization are shown in volume ratio. ^1H NMR and ^{13}C NMR spectra were obtained in $CDCl_3$ and referenced to the residual $CDCl_3$ at 7.27 ppm (^1H) and 77.0 ppm (^{13}C) unless otherwise indicated, using 300 or 500 MHz Varian instruments, and 300, 400, or 500 MHz Bruker instruments. Optical rotations were obtained using a JASCO, DIP-370 digital polarimeter at sodium D line (589 nm) using 3.5 i.d. × 50 mm cylindrical glass cell and were reported in concentration (*c* = g/100 mL) at 23 °C. Infrared (IR) spectra of neat compounds were obtained as thin films on 5 mm NaCl plates using a MIDAC Prospect FT-IR spectrophotometer. High-resolution mass spectrametric analyses were performed on Bruker Biotof II or Bruker Microtof (ESI) mass spectrometers using methanol as the solvent.



Amide 8.

To a solution of carboxylic acid **7**[1] (149 mg, 262 μmol) and amino-alcohol **6**[1] (176 mg, 261 μmol) in CH_2Cl_2 (25 mL) were added EDCI·MeI (116 mg, 390 μmol) and HOBt·H_2O (6 mg, 40 μmol). The mixture was stirred for 3 h then concentrated by rotary evaporation. The residue was purified by silica gel chromatography (hexanes–ethyl acetate, 1:1) to afford **8** (278 mg, 227 μmol, 87%) as an amorphous solid: mp 60-67 °C; R_f 0.55 (hexanes–ethyl acetate, 1:1); $[\alpha]_D^{23}$ –1.2 (*c* 1.73, $CHCl_3$); IR 3440, 3080, 2960, 1695, 1515, 1385, 1245 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.63 (d, *J* = 6.5 Hz, 2H), 7.61 (d, *J* = 7.0 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.37 (t, *J* = 7.3 Hz, 4H), 7.25 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 6.81 (ddd, *J* = 14.9, 7.4, 7.4 Hz, 1H), 6.23 (d, *J* = 9.0 Hz, 1H), 5.86 (d, *J* = 15.5 Hz, 1H), 5.33 (m, 1H), 4.78 (s, 1H), 4.76 (s, 1H), 4.60 (m, 1H), 4.44 (s, 2H), 4.27 (d, *J* = 12.0 Hz, 1H), 4.20 (m, 1H), 4.05 (m, 3H), 3.96 (m, 1H), 3.86 (m, 2H), 3.79 (s, 3H), 3.76 (d, *J* = 9.0 Hz, 1H), 3.67 (m, 2H), 3.57 (m, 1H), 3.50 (m, 1H), 3.43 (m, 1H), 3.37 (m, 1H), 3.27 (d, *J* = 10.0 Hz, 1H), 2.45 (ddd, *J* = 14.4, 7.1, 7.1 Hz, 1H), 2.39 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.26 (m, 2H), 2.01 (m, 4H), 1.77-1.17 (m, 11H), 1.43 (s, 9H), 1.26 (s, 6H), 1.09 (s, 9H), 0.94 (m, 12H), 0.75 (m, 3H), 0.59 (m, 6H); ^{13}C NMR (75 MHz) δ 165.9, 159.1, 141.6, 141.4, 135.64, 135.60, 134.0, 133.5, 130.4, 129.8, 129.7, 129.1, 127.7, 127.6, 125.2, 113.7, 110.5, 79.6, 75.3, 72.7, 71.1, 70.3, 69.9, 66.9, 65.83, 65.76, 55.2, 54.6, 52.3, 40.4, 40.2, 39.0, 38.7, 35.7, 35.4, 34.1, 32.4, 28.5, 27.0, 19.3, 6.9, 5.8, 5.0; HRMS calcd for $C_{70}H_{106}O_{12}N_2Si_2$ $[M+Na]^+$ 1245.7182, found 1245.7175. . Copies of ^{1}H NMR and ^{13}C NMR spectra of compound **8** are included below.

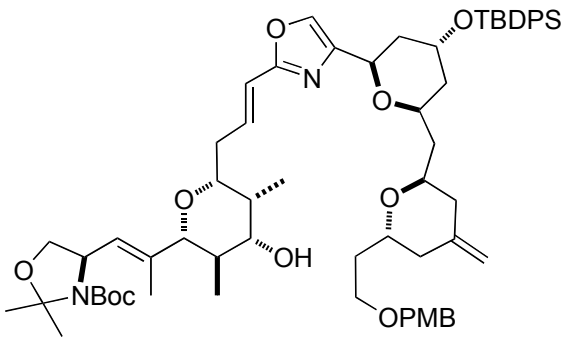
[1] Wang, B.; Hansen, T. M.; Wang, T.; Wu, D.; Weyer, L.; Ying, L.; Engler, M. M.; Sanville, M.; Leitheiser, C.; Christmann, M.; Lu, Y.; Chen, J.; Zunker, N.; Cink, R. D.; Ahmed, F.; Lee, C. S.; Forsyth, C. J. *J. Am. Chem. Soc.* **2010**, *132*, xxx.



Oxazole 10.

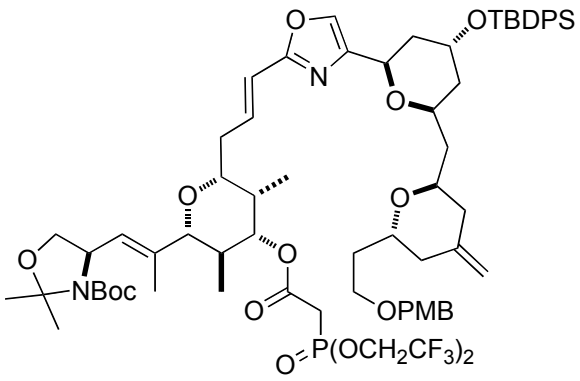
To a solution of amide **8** (145 mg, 118 μmol) in CH_2Cl_2 (2.5 mL) were added *t*-butanol (0.25 mL), $NaHCO_3$ (120 mg, 1.4 mmol) and Dess-Martin periodinane[2] (140 mg, 470 μmol). The mixture was stirred for 20 min then filtered through a plug of silica gel, eluting with hexanes : ethyl acetate (5:1 to 3:2, v/v). The eluent solution was concentrated to afford the aldehyde. This was dissolved in CH_2Cl_2 (20 mL) and Ph_3P (151 mg, 0.59 mmol), *i*-Pr_2NEt (630 μL, 2.4 mmol) and 1,2-dibromo-1,1,2,2-tetrachloroethane [$(BrCCl_2)_2$, 187 mg, 0.59 mmol] were added sequentially. The resulting mixture was stirred for 30 min before diethyl ether and saturated aqueous NH_4Cl were added. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (hexanes–ethyl acetate, 4:1) to give **10** (129 mg, 107 μmol, 91% for two steps) as an amorphous solid: mp 53-59 °C; R_f 0.65 (hexanes–ethyl acetate, 2:1); $[\alpha]_D^{23}$ +1.9 (*c* 0.83, $CHCl_3$); IR 3080, 2960, 1700, 1515, 1385, 1245 cm^{-1}; ^1H NMR (500 MHz) δ 7.67 (t, *J* = 8.0 Hz, 4H), 7.39 (m, 7H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.64 (ddd, *J* = 15.5, 8.5, 6.5 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.35 (m, 1H), 5.01 (d, *J* = 11.5 Hz, 1H), 4.76 (s, 1H), 4.72 (s, 1H), 4.62 (m, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.36 (d, *J* = 11.5 Hz, 1H), 4.31 (m, 1H), 4.19 (ddd, *J* = 11.0, 6.0, 6.0 Hz, 1H), 4.04 (m, 2H), 3.90 (dddd, *J* = 8.0, 8.0, 4.0, 4.0 Hz, 1H), 3.78 (s, 3H), 3.77 (m, 1H), 3.51 (m, 2H), 3.47 (ddd, *J* = 7.0, 7.0, 1.5 Hz, 1H), 3.40 (m, 1H), 3.29 (d, *J* = 10.0 Hz, 1H), 2.52 (ddd, *J* = 14.0, 6.8, 6.8 Hz, 1H), 2.41 (dd, *J* = 13.0, 5.0 Hz, 1H), 2.29 (m, 2H), 2.05-1.33 (m, 21H), 1.44 (s, 9H), 1.11 (s, 9H), 0.97 (m, 12H), 0.77 (m, 3H), 0.62 (m, 6H); ^{13}C NMR (75 MHz) δ 161.0, 159.0, 142.9, 142.1, 136.0, 135.7, 135.6, 134.1, 134.0, 133.8, 130.6, 129.7, 129.6, 129.1, 127.62, 127.60, 118.4, 113.7, 110.2, 79.6, 77.3, 72.6, 69.3, 69.0, 68.7, 67.5, 66.7, 65.8, 55.2, 54.6, 40.1, 39.2, 39.0, 38.8, 38.4, 37.7, 36.4, 34.4, 34.1, 28.5, 27.0, 19.3, 6.9, 5.8, 5.0; HRMS calcd for $C_{70}H_{102}O_{11}N_2Si_2$ $[M+Na]^+$ 1225.6920, found 1225.6926. Copies of ^1H NMR and ^{13}C NMR spectra of compound **10** are included below.

[2] Dess-Martin periodinane was prepared following the procedure described in: Boeckman, Jr., R. K.; Shao, P.; Mullins, J. J. *Org. Synth.* **2004**, *Coll. Vol. 10*, 696.



Alcohol 11.

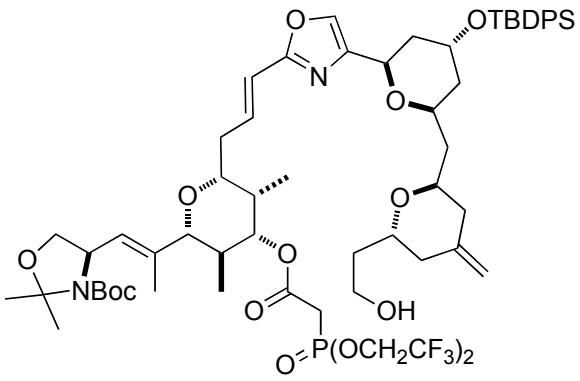
To a solution of **10** (129 mg, 107 μmol) in THF (10 mL) was added TBAF (1.0 M in THF, 214 μL, 214 μmol). The solution was stirred for 2 h before diethyl ether and saturated aqueous NH_4Cl were added. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography (hexanes–ethyl acetate, 2:1) to give **11** (110 mg, 101 μmol, 94%) as an amorphous solid: mp 65-69 °C; R_f 0.20 (hexanes–ethyl acetate, 2:1); $[\alpha]_D^{23}$ +2.3 (*c* 1.03, $CHCl_3$); IR 3470, 3070, 2930, 1730, 1690, 1380, 1240 cm^{-1}; ^1H NMR (500 MHz) δ 7.67 (t, *J* = 7.8 Hz, 4H), 7.42 (m, 3H), 7.37 (m, 4H), 7.22 (d, *J* = 8.5 Hz, 2H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.62 (ddd, *J* = 16.0, 8.0, 6.5 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.37 (m, 1H), 5.00 (d, *J* = 11.5 Hz, 1H), 4.76 (s, 1H), 4.72 (s, 1H), 4.62 (m, 1H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.31 (m, 1H), 4.18 (m, 1H), 4.04 (m, 2H), 3.90 (m, 1H), 3.78 (s, 3H), 3.77 (m, 1H), 3.51 (m, 3H), 3.42 (m, 1H), 3.32 (d, *J* = 10.0 Hz, 1H), 2.54 (ddd, *J* = 13.5, 6.5, 6.5 Hz, 1H), 2.41 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.34 (m, 1H), 2.30 (dd, *J* = 13.0, 3.5 Hz, 1H), 2.05-1.33 (m, 22H), 1.44 (s, 9H), 1.10 (s, 9H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.84 (m, 3H); ^{13}C NMR (75 MHz) δ 160.9, 159.0, 142.9, 142.1, 135.73, 135.66, 135.5, 134.2, 134.0, 133.9, 130.6, 129.71, 129.66, 129.2, 127.6, 118.6, 113.7, 110.2, 79.7, 77.3, 76.7, 72.6, 69.3, 69.0, 68.8, 67.5, 66.8, 65.8, 60.4, 55.2, 54.6, 40.1, 39.0, 38.9, 38.4, 37.9, 37.8, 36.1, 34.4, 33.8, 28.5, 27.0, 19.3, 14.2, 5.4; HRMS calcd for $C_{64}H_{88}O_{11}N_2Si$ $[M+Na]^+$ 1111.6055, found 1111.6047. Copies of ^1H NMR and ^{13}C NMR spectra of compound **11** are included below.



Phosphonate 12.

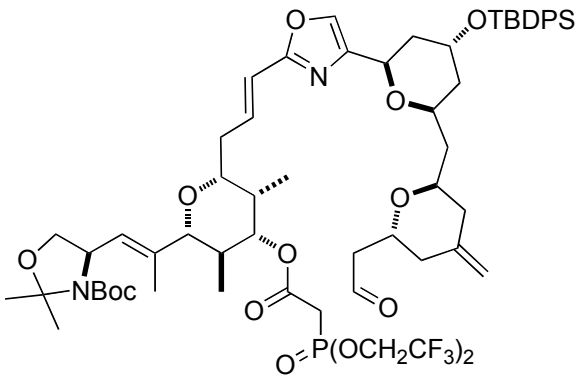
To a solution of alcohol **11** (214 mg, 196 μmol) in CH_2Cl_2 (20 mL) were added bis-(2,2,2-trifluoroethoxy)phosphono-acetic acid[3] (597 mg, 1.96 mmol), EDCI·HCl (583 mg, 1.96 mmol) and HOBt·H_2O (15 mg, 10 μmol). The mixture was stirred for 12 h before diethyl ether and saturated aqueous NH_4Cl were added. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography (hexanes–ethyl acetate, 2:1) to give **12** (248 mg, 183 μmol, 93%) as an amorphous solid: mp 50-55 °C; R_f 0.67 (hexanes–ethyl acetate, 1:1); $[\alpha]_D^{23}$ +1.3 (*c* 1.59, $CHCl_3$); IR 3070, 2940, 1735, 1690, 1510, 1385 cm^{-1}; ^{1}H NMR (500 MHz) δ 7.67 (t, *J* = 8.0 Hz, 4H), 7.39 (m, 7H), 7.23 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.5 Hz, 2H), 6.58 (ddd, *J* = 15.5, 8.5, 6.5 Hz, 1H), 6.32 (d, *J* = 16.0 Hz, 1H), 5.38 (m, 1H), 5.00 (d, *J* = 11.5 Hz, 1H), 4.76 (m, 2H), 4.71 (s, 1H), 4.61 (m, 1H), 4.46 (m, 4H), 4.40 (d, *J* = 11.5 Hz, 1H), 4.35 (d, *J* = 11.5 Hz, 1H), 4.30 (m, 1H), 4.18 (ddd, *J* = 10.5, 6.0, 6.0 Hz, 1H), 4.04 (m, 2H), 3.90 (dddd, *J* = 8.0, 8.0, 4.2, 4.2 Hz, 1H), 3.78 (s, 3H), 3.77 (m, 1H), 3.57 (ddd, *J* = 6.8, 6.8, 1.5 Hz, 1H), 3.51 (m, 2H), 3.40 (d, *J* = 10.0 Hz, 1H), 3.21 (s, 1H), 3.17 (s, 1H), 2.53 (ddd, *J* = 14.0, 6.8, 6.8 Hz, 1H), 2.40 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.30 (m, 2H), 2.12-1.33 (m, 21H), 1.43 (s, 9H), 1.10 (s, 9H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.75 (m, 3H); ^{13}C NMR (75 MHz) δ 163.9, 160.7, 159.0, 151.7, 142.9, 142.0, 135.7, 135.6, 134.9, 134.2, 134.0, 133.8, 130.6, 129.65, 129.60, 129.1, 127.6, 124.2, 124.1, 120.5, 120.4, 118.8, 113.6, 110.1, 81.0, 79.6, 76.7, 72.5, 69.3, 69.0, 68.7, 67.9, 67.4, 66.7, 65.8, 63.3, 63.2, 62.74, 62.67, 62.24, 62.17, 61.73, 61.66, 60.3, 55.1, 54.5, 40.0, 39.0, 38.8, 38.3, 37.7, 35.9, 35.2, 34.9, 34.4, 33.0, 31.3, 28.4, 27.0, 20.9, 19.2, 14.1, 5.9; HRMS calcd for $C_{70}H_{93}F_6N_2O_{15}PSi$ $[M+Na]^+$ 1397.5879, found 1397.5882. Copies of ^{1}H NMR and ^{13}C NMR spectra of compound **12** are included below.

[3] Bis-(2,2,2-trifluoroethoxy)phosphonoacetic acid was prepared in quantitative yield by hydrogenation of the corresponding benzyl ester. The benzyl ester was prepared by substituting benzyl chloroformate in the procedure described in: Patois, C.; Savignac, P.; About-Jaudet, E.; Collignon, N. *Org. Synth.* **1995**, *73*, 152-158.



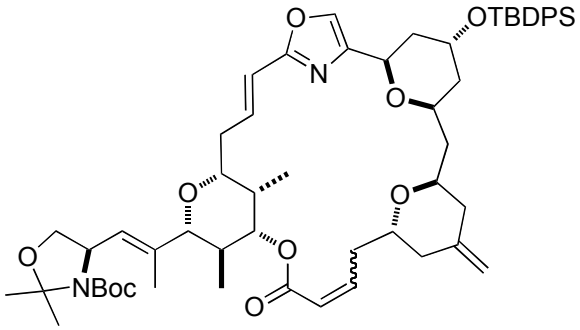
Alcohol 12a.

To a solution of **12** (140 mg, 102 μmol) in CH_2Cl_2 (23 mL) were added *t*-BuOH (2.3 mL), aqueous phosphate buffer (pH 7, 226 μL) and DDQ (230 mg, 1.04 mmol). The mixture was immersed in an aqueous sonication bath and sonicated for 1.5 min before additional phosphate buffer (226 μL, pH 7) and DDQ (230 mg, 1.04 mmol) were added and sonication continued for 2 min. Diethyl ether (80 mL) was added to the reaction mixture then it was washed with aqueous $NaHCO_3$ (30 mL), water (30 mL), and brine (30 mL). The combined aqueous washes were extracted with diethyl ether (40 mL). The combined organic phases were dried over $MgSO_4$, filtered through a plug of silica gel and concentrated by rotary evaporation. Flash chromatography (hexanes–ethyl acetate, 1:1 to 2:3) of the residue afforded **12a** (117 mg, 102 μmol, 100%) as an amorphous solid: mp 65-70 °C; R_f 0.18 (hexanes–ethyl acetate, 1:1); $[\alpha]_D^{23}$ +2.9 (*c* 1.37, $CHCl_3$); IR 3490, 3070, 2940, 1740, 1695, 1390 cm^{-1}; ^1H NMR (500 MHz) δ 7.65 (t, *J* = 8.5 Hz, 4H), 7.39 (m, 7H), 6.58 (ddd, *J* = 15.5, 8.5, 6.5 Hz, 1H), 6.31 (d, *J* = 16.0 Hz, 1H), 5.37 (m, 1H), 4.99 (dd, *J* = 11.5, 1.5 Hz, 1H), 4.76 (s, 1H), 4.73 (m, 1H), 4.71 (s, 1H), 4.60 (m, 1H), 4.45 (m, 4H), 4.32 (m, 1H), 4.17 (ddd, *J* = 10.8, 5.4, 5.4 Hz, 1H), 4.06 (m, 2H), 3.96 (dddd, *J* = 8.4, 8.4, 4.1, 4.1 Hz, 1H), 3.77 (d, *J* = 9.0 Hz, 1H), 3.69 (m, 2H), 3.57 (t, *J* = 6.5 Hz, 1H), 3.39 (d, *J* = 10.0 Hz, 1H), 3.20 (s, 1H), 3.16 (s, 1H), 2.89 (m, 1H), 2.52 (ddd, *J* = 14.0, 6.5, 6.5 Hz, 1H), 2.37 (dd, *J* = 13.2, 4.8 Hz, 1H), 2.28 (m, 2H), 2.05 (m, 4H), 1.96-1.38 (m, 17H), 1.42 (s, 9H), 1.09 (s, 9H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.75 (m, 3H); ^{13}C NMR (75 MHz) δ 163.9, 160.9, 151.7, 142.6, 141.8, 135.65, 135.63, 135.1, 134.3, 134.1, 133.8, 129.7, 127.6, 124.2, 124.1, 120.5, 120.4, 118.7, 110.3, 81.1, 79.7, 76.7, 70.3, 69.9, 69.7, 67.2, 65.8, 63.3, 63.2, 62.8, 62.7, 62.3, 62.2, 61.8, 61.7, 60.0, 54.5, 40.0, 39.0, 38.6, 38.5, 37.3, 36.2, 35.9, 35.3, 35.0, 33.1, 31.3, 28.4, 27.0, 19.3, 6.0; HRMS calcd for $C_{62}H_{85}F_6N_2O_{14}PSi$ $[M+Na]^+$ 1277.5310, found 1277.5315. Copies of ^1H NMR and ^{13}C NMR spectra of compound **12a** are included below.



Aldehyde 5.

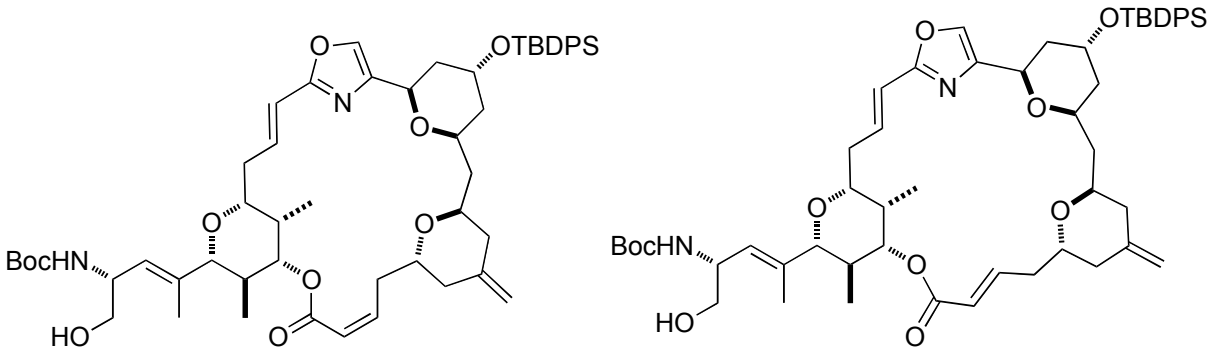
To a stirred, 0 °C solution of **12a** (100 mg, 800 μmol) in CH_2Cl_2 (2 mL) were added $NaHCO_3$ (500 mg, 6.0 mmol) and Dess-Martin periodinane[4] (460 mg, 1.1 mmol). The cold bath was removed and the mixture was stirred for 20 min. The mixture was filtered through silica gel, eluting with hexanes–EtOAc (4:1), and the eluant was concentrated to give the derived aldehyde **5** (100 mg, 80 μmol, 100%) as an amorphous solid: mp 68-72 °C; R_f 0.21 (hexanes–ethyl acetate, 2:1); IR 3070, 2930, 2860, 2730, 1725, 1695, 1385 cm^{-1}; ^1H NMR (500 MHz) δ 9.71 (t, *J* = 2.3 Hz, 1H), 7.66 (t, *J* = 7.8 Hz, 4H), 7.42 (m, 3H), 7.37 (m, 4H), 6.59 (ddd, *J* = 15.6, 8.4, 6.5 Hz, 1H), 6.33 (d, *J* = 16.0 Hz, 1H), 5.38 (m, 1H), 5.01 (d, *J* = 12 Hz, 1H), 4.80 (s, 1H), 4.77 (s, 1H), 4.75 (m, 1H), 4.62 (m, 1H), 4.46 (m, 4H), 4.31 (m, 2H), 4.18 (m, 1H), 4.06 (m, 1H), 4.01 (m, 1H), 3.77 (d, *J* = 8.5 Hz, 1H), 3.57 (ddd, *J* = 7.0, 7.0, 1.5 Hz, 1H), 3.39 (d, *J* = 11.0 Hz, 1H), 3.21 (s, 1H), 3.17 (s, 1H), 2.57 (ddd, *J* = 16.0, 7.0, 2.5 Hz, 1H), 2.52 (m, 1H), 2.48 (ddd, *J* = 16.5, 6.0, 2.0 Hz, 1H), 2.41 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.37 (dd, *J* = 13.0, 3.5 Hz, 1H), 2.30 (ddd, *J* = 14.3, 7.3, 7.3 Hz, 1H), 2.10-1.86 (m, 7H), 1.80-1.31 (m, 12H), 1.43 (s, 9H), 1.09 (s, 9H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.75 (m, 3H); HRMS calcd for $C_{62}H_{83}F_6N_2O_{14}PSi$ $[M+Na]^+$ 1275.5153, found 1275.5155. A copy of the ^1H NMR spectrum compound **5** is included below.



Macrolides 14 and **15** (**14** : **15** = 4 : 1).

To a solution of 18-crown-6 (307 mg, 1.13 mmol) in toluene (98 mL) was added K_2CO_3 (80 mg, 0.47 mmol), and the resulting suspension was stirred for 3 h, before a solution of **5** (120 mg, 95.7 μmol) in toluene (98 mL) was added. After stirring for 9 h, the mixture was diluted by diethyl ether (50 mL), washed with water (30 mL), and brine (30 mL). The separated aqueous phase was extracted with diethyl ether (3 × 50 mL) and the combined

organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate–CH_2Cl_2, 3:1:1) to afford a 4:1 mixture of (2*Z*)-**14**/(2*E*)-**15** (88 mg, 88.7 μmol, 93%): R_f 0.21 (hexanes–ethyl acetate, 2:1); HRMS calcd for $C_{58}H_{78}F_6N_2O_{10}Si$ $[M+Na]^+$ 1013.5318, found 1013.5324. A copy of the ^1H NMR spectrum of the mixture of compounds **14** and **15** (**14** : **15** = 4 : 1) is included below.



Alcohols 16 and 17.

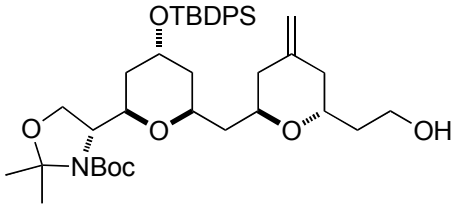
To a solution of **14** and **15** (**14** : **15** = 4 : 1, 73.4 mg, 74.0 μmol) in methanol (50 mL) was added *p*-TsOH·H_2O (58.3 mg, 250 μmol). The resulting solution was stirred for 3 h. Ethyl acetate (180 mL) was added and the resulting mixture was washed with saturated aqueous $NaHCO_3$ (20 mL), and brine (20 mL), and the combined aqueous phases were extracted with ethyl acetate (2 × 20 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated by rotary evaporation. The residue was eluted through a pad of silica gel, with ethyl acetate to afforded a mixture of (2*Z*)-**16** and (2*E*)-**17** (**16** : **17** = 4 : 1, 57 mg, 60.0 μmol, 81%). Compounds **16** and **17** were initially purified by flash column chromatography then separated by preparative TLC (hexanes–ethyl acetate–CH_2Cl_2, 2:2:1). A sample of **16** was recrystallized from hexanes–ethyl acetate (4:1) for X-ray analysis.[4]

Analytical data for **16**: mp 182-184 °C; R_f 0.31 (hexanes–ethyl acetate, 1:1); $[\alpha]_D^{23}$ +20.8 (*c* 1.50, $CHCl_3$); IR 3390, 3070, 2920, 1705 cm^{-1}; ^1H NMR (500 MHz) δ 7.64 (t, *J* = 8.0 Hz, 4H), 7.40 (m, 7H), 6.71 (ddd, *J* = 16.0, 10.0, 6.0 Hz, 1H), 6.30 (d, *J* = 16.0 Hz, 1H), 5.93 (m, 2H), 5.32 (d, *J* = 9.0 Hz, 1H), 5.03 (s, 1H), 4.96 (m, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.64 (s, 1H), 4.47 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.43 (m, 1H), 4.33 (m, 1H), 4.20 (m, 2H), 3.98 (m, 1H), 3.47 (m, 5H), 2.77 (d, *J* = 12.0 Hz, 1H), 2.55 (m, 2H), 2.41 (m, 3H), 2.29 (m, 1H), 2.08 (d, *J* = 13.5 Hz, 1H), 1.95 (m, 3H), 1.84 (ddd, *J* = 12.5, 12.5, 5.0 Hz, 1H), 1.77 (s, 3H), 1.75 (m, 1H), 1.54 (d, *J* = 15.0 Hz, 1H), 1.43 (s, 9H), 1.35 (m, 2H), 1.08 (s, 9H), 0.96 (d, *J* = 7.5 Hz, 3H), 0.73 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (75 MHz) δ 165.8, 161.3, 144.7, 142.2, 141.8, 137.0, 135.7, 134.1, 133.9, 133.8, 129.80, 129.76, 127.7, 126.9, 120.9, 119.3, 110.1, 89.2, 79.6, 78.1, 73.4, 69.0, 67.3, 65.8, 65.3, 50.6, 41.2, 39.2, 38.9, 37.0, 35.1, 34.4,

[4] Forsyth, C. J.; Ahmed, F.; Cink, R. D.; Lee, C. S. *J. Am. Chem. Soc.* **1998**, *120*, 5597-5598.

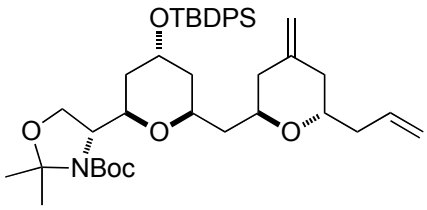
32.5, 31.1, 30.3, 28.3, 27.0, 19.3, 13.3, 11.8, 6.0.; HRMS calcd for $C_{55}H_{74}N_2O_{10}Si$ $[M+Na]^+$ 973.5005, found 973.5009. Copies of ^1H NMR and ^{13}C NMR spectra of compound **16** are included below.

Analytical data for **17**: R_f 0.35 (hexanes–ethyl acetate, 1:1); $[\alpha]_D^{23}$ +13.3 (*c* 1.9, $CHCl_3$); IR 3385, 3062, 2913, 1702 cm^{-1}; ^1H NMR (500 MHz) δ 7.68 (m, 4H), 7.44 (m, 7H), 7.00 (m, 1H), 6.66 (m, 1H), 6.25 (d, *J* = 16.2 Hz, 1H), 5.93 (d, *J* = 15.3 Hz, 1H), 5.72 (d, *J* = 7.2 Hz, 1H), 5.64 (dd, *J* = 8.7 Hz, 1H), 5.06 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.93 (m, 2H), 4.82 (s, 1H), 4.54 (m, 1H), 4.34 (m, 1H), 3.89 (m, 1H), 3.80-3.40 (m, 5H), 2.64 (d, *J* = 12.9 Hz, 1H), 2.53 (dd, *J* = 12.9, 4.8 Hz, 1H), 2.33 (m, 4H), 2.04 (m, 4H), 1.81 (s, 3H), 1.66 (d, *J* = 12.3 Hz, 2H), 1.47 (m, 12H), 1.16 (s, 9H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.80 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (75 MHz) δ 167.3, 161.3, 155.7, 147.8, 141.9, 141.6, 135.5, 135.3, 134.0, 133.8, 133.7, 129.7, 128.4, 127.6, 127.59, 125.4, 122.2, 117.7, 111.0, 90.1, 78.8, 77.1, 70.4, 69.9, 68.4, 67.4, 66.1, 65.4, 65.0, 56.0, 49.6, 40.6, 40.1, 38.6, 37.9, 36.8, 34.9, 34.9, 34.8, 31.3, 30.2, 29.6, 28.3, 27.0, 19.3, 13.2, 11.5, 5.7; HRMS calcd for $C_{55}H_{74}N_2O_{10}Si$ $[M+Na]^+$ 973.5005, found 973.5005. Copies of ^1H NMR and ^{13}C NMR spectra of compound **17**are included below.



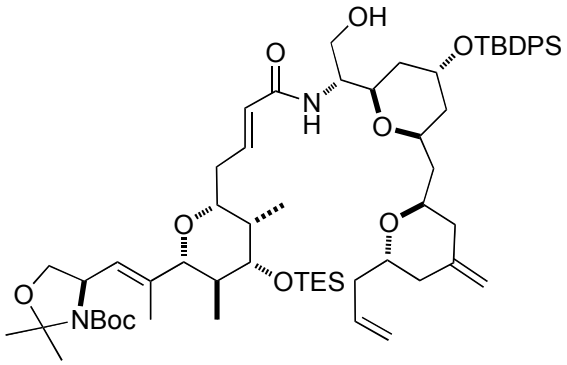
Alcohol 51.

To a solution of PMB ether **20**[1] (171 mg, 210 μmol) in CH_2Cl_2 (2 mL) were added *t*-BuOH (0.2 mL), aqueous phosphate buffer (pH 7, 0.2 mL), and DDQ (95 mg, 0.42 mmol). The mixture was immersed in an aqueous sonication bath and sonicated for 5 min before saturated aqueous $NaHCO_3$ and diethyl ether were added. The separated aqueous phase was extracted with diethyl ether and the combined organic phase was washed with brine, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate, 3:2) to give **51** (140 mg, 202 μmol, 96 %) as a colorless oil. R_f 0.26 (hexanes–ethyl, 7:3 acetate); $[\alpha]_D^{23}$ +1.1 (*c* 0.93, $CHCl_3$); IR 3490, 3072, 2933, 2858, 1700, 1398, 1105 cm^{-1}; ^1H NMR (500 MHz, a mixture of carbamate rotamers) δ 7.63 (m, 4H), 7.37 (m, 6H), 4.79 (s, 1H), 4.74 (s, 1H), 4.41-4.30 (d, *J* = 12.0 Hz, 1H), 4.26 (m, 1H), 4.10 (m, 1H), 4.04 (m, 1H), 3.98-3.94 (m, 2H), 3.86 (dd, *J* = 6.5, 9.0 Hz, 1H), 3.71 (m, 2H), 2.41 (d, *J* = 12.5 Hz, 1H), 2.29 (dt, *J* = 13.0, 3.5 Hz, 1H), 2.06 (m, 2H), 1.83 (m, 1H), 1.78 (dt, *J* = 7.5, 6.5 Hz, 1H), 1.63-1.43 (m, 21H), 1.32 (q, *J* = 12.0 Hz, 2H), 1.08 (d, *J* = 6.0 Hz, 9H); ^{13}C NMR (125 MHz, a mixture of carbamate rotamers) δ 152.6, 141.8, 135.8, 135.6, 133.8, 110.4, 93.9, 93.4, 80.3, 79.9, 71.1, 70.3, 69.8, 65.9, 63.6, 63.4, 60.8, 60.3, 59.3, 56.6, 40.3, 39.5, 38.7, 38.4, 36.5, 36.3, 32.7, 32.4, 28.4, 27.1, 27.0, 26.7, 25.9, 23.9, 22.5, 21.9, 19.4, 19.3, 14.2 1.1; HRMS calc. for $C_{40}H_{59}NO_7Si$ $[M+Na]^+$ 716.3959, found 716.3961. Copies of ^1H NMR and ^{13}C NMR spectra of compound **51** are included below.



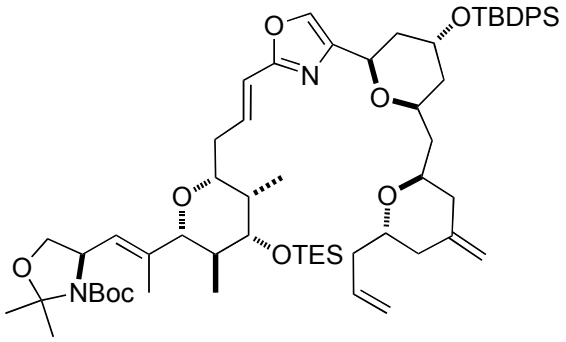
Alkene 21.

Alcohol **51** (140 mg, 202 μmol) was dissolved in CH_2Cl_2 (4 mL) and cooled to 0 °C. $NaHCO_3$ (125 mg, 1.50 mmol) and Dess-Martin periodinane (300 mg, 700 μmol) were added. The cold bath was removed and the mixture was stirred for 20 min. Then the mixture was filtered through silica gel, eluted with hexanes and ethyl acetate (hexanes–ethyl acetate, 4:1), and the filtrate was concentrated to give the aldehyde as a colorless oil. To a 0 °C suspension of Ph_3PCH_3Br (536 mg, 1.45 mmol) in THF (5 mL) was added a solution of *n*-BuLi (0.57 mL, 1.4 mmol, 2.5 M in hexane) dropwise. The resulting orange mixture was stirred for 5 min before being warmed to rt then stirred for 30 min. A solution of the aldehyde in THF (2.5 mL) was added via cannula. The reaction mixture was stirred at rt for 10 min before saturated aqueous NH_4Cl and diethyl ether were added. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate, 9:1) to give **21** (131 mg, 190 μmol, 94%) as a colorless oil: R_f 0.42 (hexanes–ethyl acetate, 9:1); $[\alpha]_D^{23}$ –4.0 (*c* 4.9, $CHCl_3$); IR 3072, 2933, 2858, 1700, 1386, 1365, 1094 cm^{-1}; ^1H NMR (500 MHz, a mixture of carbamate rotamers) δ 7.65 (m, 4H), 7.38 (m, 6H), 5.79 (ddt, *J* = 18.5, 10.0, 7.5 Hz, 1H), 5.06 (d, *J* = 18.5 Hz, 1H), 5.03 (d, *J* = 10.0 Hz, 1H), 4.79 (s, 1H), 4.76 (s, 1H), 4.46-4.32 (m, 1H), 4.26 (d, *J* = 13 Hz, 1H), 4.11-3.96 (m, 4H), 3.85 (dd, *J* = 9.0, 6.0 Hz, 1H), 3.82-3.78 (m, 1H), 2.40 (dd, *J* = 13.5, 4.0 Hz, 1H), 2.34-2.23 (m, 2H), 2.23 (dt, *J* = 14.5, 7.0 Hz, 1H), 2.04 (dd, *J* = 12.5, 6.0 Hz, 2H), 1.86 (dt, *J* = 14.0, 7.0 Hz, 1H), 1.78 (m, 1H), 1.64 (d, *J* = 13.5 Hz, 1H), 1.58 (d, *J* = 14.0 Hz, 1H), 1.51-1.43 (m, 15H), 1.33-1.27 (m, 2H), 1.09 (s, 9H); ^{13}C NMR (125 MHz, a mixture of carbamate rotamers) δ 152.4, 142.2, 135.9, 135.7, 134.9, 134.1, 133.8, 129.6, 129.5, 127.8, 127.6, 116.9, 110.3, 93.9, 93.4, 81.1, 80.6, 80.1, 79.8, 79.1, 73.2, 71.6, 71.3, 70.9, 69.8, 69.3, 69.0, 66.0, 63.5, 63.3, 59.4, 39.2, 39.1, 39.0, 38.7, 38.4, 32.7, 32.3, 28.4, 27.1, 27.0, 25.9, 23.8, 22.4, 19.4, 19.3; HRMS calc. for $C_{41}H_{59}NO_6Si$ $[M+Na]^+$ 712.4009, found 712.4010. Copies of ^1H NMR and ^{13}C NMR spectra of compound **21** are included below.



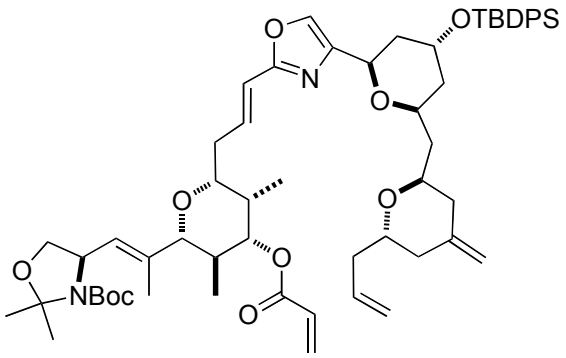
Amide 23.

To MeOH (0.5 mL) at 0 °C, was added acetyl chloride (20 μL). After stirring for 20 min, this mixture was added to diene **21** (35 mg, 50 μmol). After stirring at 0 °C for 2 h, the solvent was removed under a gentle flow of N_2. The residue was dried in high vacuum for 1 h, dissolved CH_2Cl_2 (0.5 mL) and treated with *i*-Pr_2NEt (30 μL, 110 μmol). Then carboxylic acid **7**[1] (28 mg, 50 μmol) in CH_2Cl_2 (0.5 mL) was added followed by EDCI·HCl (14 mg, 75 μmol) and HOBt·H_2O (1.5 mg, 9 μmol). The resulting mixture was stirred for 10 h. Separation of this mixture directly by flash chromatography (hexanes–ethyl acetate, 4:1 to 1:1) to give compound **23** (44 mg, 40 μmol, 80%) as a colorless oil: R_f 0.58 (hexanes–ethyl acetate, 1:1); $[\alpha]_D^{23}$ –1.4 (*c* 0.86, $CHCl_3$); IR 3436, 3073, 2956, 2877, 1700, 1387, 1105, 1077 cm^{-1}; ^1H NMR (500 MHz, a mixture of carbamate rotamers) δ 7.66 (m, 4H), 7.45-7.35 (m, 7H), 6.80 (dt, *J* = 15.0, 8.5 Hz, 1H), 6.26 (d, *J* = 8.5 Hz, 1H), 5.87 (d, *J* = 15.5 Hz, 1H), 5.82 (m, 1H), 5.36-5.28 (m, 1H), 5.12 (dd, *J* = 14.5 Hz, 1H), 5.09 (d, *J* = 11.0 Hz, 1H),4.80 (s, 1H), 4.76 (s, 1H), 4.63-4.56 (m, 1H), 4.26 (d, *J* = 11.5 Hz, 1H), 4.19 (m, 1H), 4.02 (m, 3H), 3.96 (m, 2H), 3.83 (m, 2H), 3.76 (d, *J* = 8.5 Hz, 1H), 3.69 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.43 (dt, *J* = 7.5, 1.5 Hz, 1H), 3.36 (m, 1H), 3.27 (d, *J* = 10.0 Hz, 1H), 2.47 (m, 1H), 2.42 (dd, *J* = 13.5, 5.0 Hz, 1H), 2.25 (d, *J* = 14.5 Hz, 1H), 2.19 (m, 1H), 2.06 (d, *J* = 13.0 Hz, 1H), 1.99 (m, 1H), 1.74-1.62 (m, 3H), 1.56-1.36 (m, 12H), 1.43 (s, 9H), 1.36-1.25 (m, 3H), 1.19 (t, *J* = 4.0 Hz, 1H), 1.08 (s, 9H), 0.94 (m, 12H), 0.77 (m, 3H), 0.59 (m, 6H); ^{13}C NMR (75 MHz, a mixture of carbamate rotamers) (partial) δ 165.8, 141.7, 141.3, 135.7, 135.6, 135.2, 134.1, 133.7, 129.8, 129.7, 125.3, 116.7, 110.6, 80.4, 80.0, 79.9, 79.7, 75.6, 72.0, 71.4, 70.5, 66.1, 65.9, 54.6, 52.2, 41.0, 40.7, 39.5, 39.1, 38.8, 38.1, 36.5, 35.8, 35.4, 34.1, 29.7, 28.6, 27.0, 23.6, 22.7, 19.3, 14.2, 11.6, 7.1, 7.0, 6.1, 5.8, 5.7, 5.1, 5.0. HRMS calc. for $C_{63}H_{98}N_2O_{10}Si_2$ $[M+Na]^+$ 1121.6658, found 1121.6654. Copies of ^1H NMR and ^{13}C NMR spectra of compound **23** are included below.



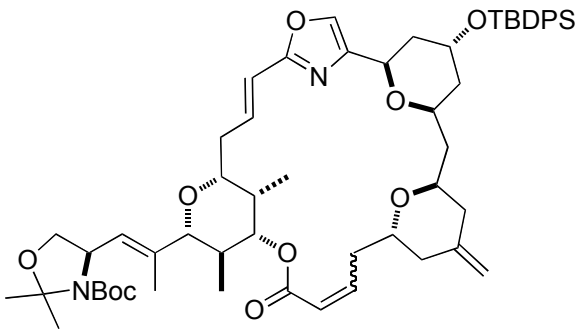
Oxazole 24.

To a solution of amide **23** (44 mg, 40 μmol) in CH_2Cl_2 (1 mL) were added *t*-BuOH (0.1 mL), $NaHCO_3$ (32 mg, 0.38 mmol) and Dess-Martin periodinane[2] (48 mg, 0.16 mmol). The mixture was stirred for 20 min then filtered through a plug of silica gel, eluting with hexanes–ethyl acetate (5:1 to 3:2). Concentration of the eluent gave an *N*-acyl-α-aminoaldehyde, which was dissolved in CH_2Cl_2 (2 mL). Ph_3P (52 mg, 0.20 mmol), *i*-Pr_2NEt (220 μL, 0.83 mmol) and $(BrCCl_2)_2$ (65 mg, 0.20 mmol) were added sequentially. The resulting mixture was stirred for 30 min before diethyl ether and saturated aqueous NH_4Cl were added. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (hexanes–ethyl acetate, 4:1) to give compound **24** (38 mg, 35 μmol, 87%) as an oil: R_f 0.57 (hexanes–ethyl acetate, 4:1); $[\alpha]_D^{23}$ –19.1 (*c* 2.8, $CHCl_3$); IR 3072, 3048, 2955, 2876, 2861, 1700, 1387, 1105, 1078 cm^{-1}; ^1H NMR (500 MHz, a mixture of carbamate rotamers) δ 7.67 (m, 4H), 7.38 (m, 6H), 6.62 (ddd, *J* = 15.0, 8.5, 6.5 Hz, 1H), 6.56 (s, 1H), 6.32 (d, *J* = 15.0 Hz, 1H); 5.78 (ddd, *J* = 18.5, 10.0, 7.5 Hz, 1H), 5.39-5.32 (m, 1H), 5.07 (d, *J* = 18.5 Hz, 1H), 5.02 (d, *J* = 10.0 Hz, 1H), 4.77 (s, 1H), 4.75 (s, 1H), 4.66-4.58 (m, 1H), 4.31 (m, 1H), 4.23 (m, 1H), 4.03 (m, 2H), 3.79 (m, 2H), 3.46 (ddt, *J* = 19.0, 11.5, 6.5 Hz, 1H), 3.40 (m, 1H), 3.30 (t, *J* =10.5 Hz, 1H), 2.51 (m, 1H), 2.40 (dd, *J* = 13.5, 4.5 Hz, 1H), 2.35-2.27 (m, 4H), 2.22 (m, 2H), 2.02 (m, 4H), 1.78-1.22 (m, 23H), 1.10 (d, *J* = 7.5 Hz, 9H), 0.96 (m, 12H), 0.79 (m, 3H), 0.62 (m, 6H), ^{13}C NMR (75 MHz, a mixture of carbamate rotamers) δ 161.0, 151.7, 142.8, 142.0, 136.0, 135.7, 135.6, 134.7, 134.1, 133.9, 133.7, 129.6, 127.6, 118.3, 116.8, 110.2, 93.7, 88.4, 82.6, 80.8, 79.6, 79.1, 71.7, 71.5, 70.9, 69.2, 68.9, 68.0, 67.2, 65.6, 54.5, 42.4, 40.3, 39.1, 39.0, 38.9, 38.7, 38.1, 38.0, 37.5, 36.3, 34.0, 33.5, 28.4, 26.9, 24.9, 23.4, 19.2, 13.8, 13.6, 13.1, 11.4, 6.9, 6.8, 5.6, 5.5, 4.8; HRMS calc. for $C_{63}H_{94}N_2O_9Si_2$ $[M+Na]^+$ 1101.6396, found 1101.6625. Copies of ^1H NMR and ^{13}C NMR spectra of compound **24** are included below.



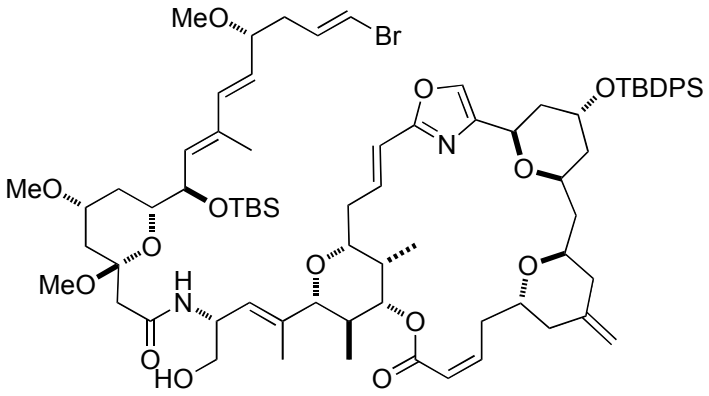
Acrylate 19.

To a solution of oxazole **24** (10 mg, 9.5 μmol) in THF (0.2 mL) was added TBAF (50 μL, 50 μmol, 1 M in THF). The mixture was stirred for 10 min and then filtered through a plug of silica gel, eluting with hexanes–ethyl acetate (3:1) to give an alcohol. To a solution of acryloyl chloride (40 μL, 0.5 mmol) in CH_2Cl_2 (1 mL), at 0 °C, was added *i*-Pr_2NEt (180 μL, 1 mmol), and stirred 5 min. Then the alcohol in CH_2Cl_2 (0.2 mL) was added. The resulting mixture was stirred at 0 °C for 10 min before saturated aqueous $NaHCO_3$ was added. The separated aqueous phase was extracted with diethyl ether, and the combined organic phase was washed with brine, dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography to give compound **19** (9.5 mg, 9.3 μmol, 98 %) as an oil: R_f 0.60 (hexanes–ethyl acetate, 7:3); $[\alpha]_D^{23}$ +5.6 (*c* 0.43, $CHCl_3$); IR 3073, 2933, 2859, 1726, 1696, 1390, 1367, 1265, 1190, 1105 cm^{-1}; ^1H NMR (500 MHz, a mixture of carbamate rotamers) δ 7.67 (t, *J* = 8.0 Hz, 4H), 7.45-7.35 (m, 7H), 6.60 (ddd, *J* = 15.5, 8.5, 6.5 Hz, 1H), 6.43 (d, *J* = 17.5 Hz, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.14 (dd, *J* = 17.5, 16.0 Hz, 1H), 5.85 (d, *J* = 15.5 Hz, 1H), 5.79 (ddt, *J* = 17.0, 9.5, 7.5 Hz, 1H), 5.43-5.32 (m, 1H), 5.05 (d, *J* =17.0 Hz, 1H), 5.01 (d, *J* = 9.5 Hz, 1H), 4.76 (s, *1*H), 4.73 (s, *1*H), 4.65-4.58 (m, 1H), 4.31 (m, 1H), 4.21 (m, 1H), 4.06 (m, 1H), 4.00 (dd, *J* = 13.0, 5.0 Hz, 1H), 3.78 (m, 2H), 3.62 (m, 1H), 3.42 (d, *J* = 10.5 Hz, 1H), 2.54 (m, 1H), 2.40 (dd, *J* = 13.5, 5.0 Hz, 1H), 2.34-2.28 (m, 2H), 2.22 (q, *J* = 7.0 Hz, 1H), 2.11 (m, 1H), 2.06-1.98 (m, 3H), 1.88 (d, *J* = 13.0 Hz, 1H), 1.79-1.63 (m, 6H), 1.43 (m, 12H), 1.26 (s, 3H), 1.10 (s, 9H), 0.80 (d, *J* = 7.0 Hz, 3H), 0.78-0.66 (m, 6H); ^{13}C NMR (75 MHz, a mixture of carbamate rotamers) δ 165.3, 160.8, 142.8, 142.0, 135.7, 135.6, 135.2, 134.7, 134.1, 133.9, 133.8, 130.8, 129.6, 128.4, 127.5, 118.6, 116.8, 79.6, 79.0, 78.6, 76.7, 70.9, 69.2, 68.9, 67.2, 65.6, 54.5, 39.9, 39.1, 39.0, 38.6, 38.0, 37.5, 35.9, 35.1, 31.8, 31.4, 30.2, 29.5, 28.4, 28.2, 26.9, 24.9, 22.5, 19.2, 14.0, 12.7, 11.1, 6.0, 0.8.; HRMS calc. for $C_{60}H_{82}N_2O_{10}Si$ $[M+Na]^+$ 1041.5636, found 1041.5633. Copies of ^1H NMR and ^{13}C NMR spectra of compound **19** are included below.



Macrolides 14 and 15 (14 : 15 > 10 : 1)

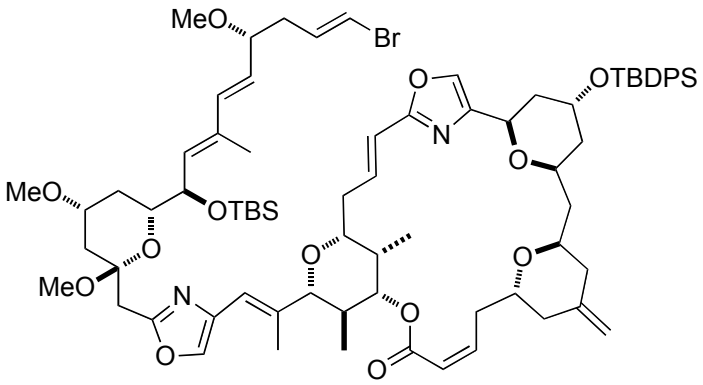
Preparation of **14** and **15** in hexane: To a solution of acrylate **19** (2.9 mg, 2.7 μmol) in argon-purged *n*-hexane (29 mL) at reflux was added a solution of Grubbs' second generation catalyst (0.6 mg, 0.7 μmol) in hexane (1 mL) dropwise over 45 min. The solution was maintained at reflux for an additional 15 min before it was cooled to 0 °C and filtered through a pad of silica gel. The filtrate was concentrated and chromatographed (hexanes–ethyl acetate, 6:1 to 4:1) to give a mixture of **14** and **15** (1.9 mg, 1.7 μmol, 65%, > 10 : 1 ratio of **14** : **15** as assayed by ^{1}H NMR spectroscopy). IR 3073, 2933, 2859, 1726, 1696, 1390, 1367, 1190, 1105 cm^{-1}; HRMS calc. for $C_{60}H_{82}N_2O_{10}Si$ $[M+Na]^+$ 1041.5636, found 1041.5633; A copy of the ^{1}H NMR spectrum of the mixture of **14** and **15** (**14** : **15** > 10 : 1) thus prepared is included below.



(2*Z*)-Amide (26).

To a solution of (2*Z*)-macrolide **16** (2.0 mg, 2.1 μmol) in CH_2Cl_2 (0.5 mL) was added TFA (50 μL). The solution was stirred for 30 min before the volatile components were removed under a stream of dry nitrogen. The residue was concentrated under high vacuum for 1 h before an aqueous phosphate buffer (pH 5.7, 0.5 mL) was added. The mixture was stirred for 30 min before it was extracted with diethyl ether (5 × 2 mL). The combined extracts were dried over Na_2SO_4, filtered, and concentrated to give the crude ammonium salt. To a stirred solution of acid **7**[1] (1.3 mg, 2.1 μmol) in CH_2Cl_2 (0.5 mL) was added (7-azabenzotriazol-1-yloxy)-tris(pyrrolidino)phosphonium hexafluorophosphate (PyAOP, 1.1 mg, 2.1 μmol) and *i*-Pr_2NEt (1.1 μL, 6.2 μmol). The mixture was stirred for 1 min before a solution of the crude ammonium salt in CH_2Cl_2 (0.5 mL)

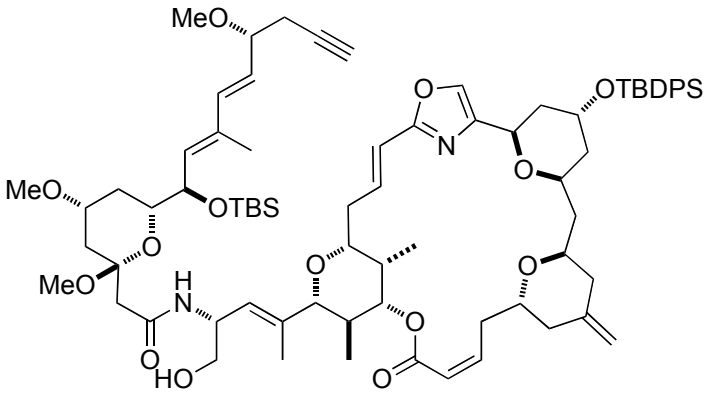
was added. The reaction mixture was stirred for 1 h before diethyl ether (1 mL) was added and the resultant mixture washed with saturated aqueous $NaHCO_3$ (1 mL). The aqueous phase was extracted with diethyl ether (2 × 1 mL), and the combined organic phase was dried over Na_2SO_4, filtered, and concentrated. Silica gel column chromatography (hexanes–ethyl acetate, 1:1 to 1:2) of the residue gave hydroxy amide **26** (2.5 mg, 1.8 μmol, 85%) as white film: R_f 0.51 (ethyl acetate); $[\alpha]_D^{23}$ +19 (c 0.25, $CHCl_3$); ^{1}H NMR (500 MHz) δ 7.65 (t, *J* = 7.8 Hz, 4H), 7.40 (m, 7H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.71 (ddd, *J* = 16.0, 10.0, 6.0 Hz, 1H), 6.29 (d, *J* = 16.0 Hz, 1H), 6.19 (m, 2H), 6.10 (dd, *J* = 13.5, 1.0 Hz, 1H), 5.92 (m, 2H), 5.48 (dd, *J* = 15.8, 7.7 Hz, 1H), 5.40 (m, 1H), 5.03 (s, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.78 (m, 1H), 4.65 (s, 1H), 4.50 (dd, *J* = 9.5, 7.0 Hz, 1H), 4.47 (dd, *J* = 11.5, 4.5 Hz, 1H), 4.33 (m, 1H), 4.20 (m, 2H), 3.98 (m, 1H), 3.74 (dd, *J* = 11.0, 4.0 Hz, 1H), 3.65 (m, 2H), 3.60 (m, 1H), 3.50 (m, 3H), 3.43 (d, *J* = 10.0 Hz, 1H), 3.30 (s, 3H), 3.27 (s, 3H), 3.20 (s, 3H), 2.77 (d, *J* = 12.0 Hz, 1H), 2.74 (d, *J* = 14.5 Hz, 1H), 2.52 (m, 1H), 2.50 (d, *J* = 14.5 Hz, 1H), 2.42 (m, 2H), 2.29 (m, 5H), 2.08 (d, *J* = 15.0 Hz 1H), 1.91 (m, 5H), 1.80 (d, *J* = 1.0 Hz, 1H), 1.79 (d, *J* = 1.0 Hz, 1H), 1.74 (m, 1H), 1.55 (d, *J* = 14.0 Hz, 1H), 1.36 (m, 3H), 1.12 (m, 1H), 1.08 (s, 9H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.88 (s, 9H), 0.72 (d, *J* = 6.5 Hz, 3H), 0.07 (s, 3H), 0.03 (s, 3H); HRMS calc. for $C_{76}H_{109}N_2O_{14}Si_2Br$ $[M+Na]^+$ 1431.6498, found 1431.6597. A copy of ^{1}H NMR spectrum of compound **26** is included below.



(2*Z*)-Bisoxazole (27).

$NaHCO_3$ (100 mg, 127 μmol), Dess-Martin periodinane[2] (50 mg, 80 μmol), and *t*-butanol (25 μL) were stirred in CH_2Cl_2 (2.85 mL) for 5 min then cooled to 0 °C. A pre-cooled solution of amide **26** (5.7 mg, 4.0 μmol) in CH_2Cl_2 (1.0 mL) was added. After stirring for 45 min, approximately one-half of the CH_2Cl_2 solvent was evaporated from the reaction mixture with a stream of N_2, and the volume was made up with diethyl ether. Dissolution was ensured by use of sonication. Flash column chromatography (diethyl ether) of the mixture gave the aldehyde free of Dess-Martin periodinane derived impurities. The diethyl ether was removed under a stream of N_2, and the aldehyde was placed on the high vacuum for 30 min. To this crude aldehyde in CH_2Cl_2 (3.0 mL) was sequentially added Ph_3P (10 mg, 12.2 μmol), *i*-Pr_2NEt (28 μL, 159 μmol) and $(BrCCl_2)_2$ (12.7 mg, 12.2 μmol). The mixture was stirred for 9 h before additional *i*-Pr_2NEt (50 μL) was added. After 2.5 h, the solution

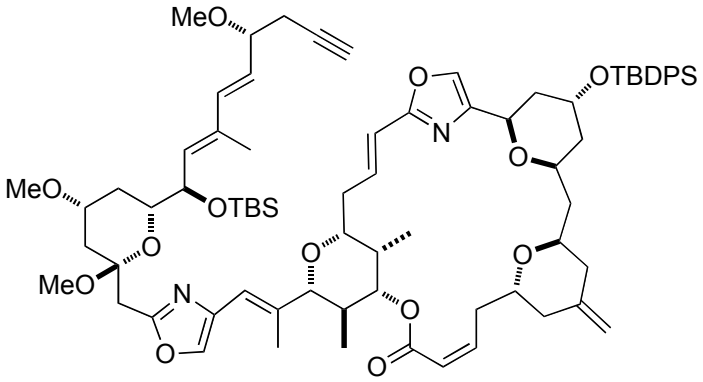
was diluted with diethyl ether and saturated aqueous NH_4Cl. The separated aqueous phase was extracted with diethyl ether (3 × 5 mL). The combined organic phase was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (hexanes–ethyl acetate, 2:1) to give bisoxazole **27** (4.0 mg, 2.8 μmol, 71% for two steps) as a white film: R_f 0.33 (hexanes–ethyl acetate, 3:2); $[\alpha]_D^{23}$ +43.0 (c 0.07, $CHCl_3$); IR 3070, 2925, 2850, 1735, 1715, 1180, 1090 cm^{-1}; ^1H NMR (500 MHz) δ 7.65 (t, *J* = 8.0 Hz, 4H), 7.55 (s, 1H), 7.40 (m, 7H), 6.72 (ddd, *J* = 16.0, 10.0, 6.5 Hz, 1H), 6.31 (d, *J* = 15.5 Hz, 1H), 6.28 (s, 1H), 6.19 (m, 2H), 6.10 (dd, *J* = 13.5, 1.0 Hz, 1H), 5.92 (m, 2H), 5.46 (dd, *J* = 15.8, 7.7 Hz, 1H), 5.40 (d, *J* = 9.0 Hz, 1H), 5.04 (s, 1H), 4.91 (d, *J* = 12.0 Hz, 1H), 4.66 (s, 1H), 4.53 (dd, *J* = 11.3, 4.2 Hz, 1H), 4.43 (dd, *J* = 9.5, 7.0 Hz, 1H), 4.33 (m, 1H), 4.20 (m, 2H), 3.99 (m, 1H), 3.65 (q, *J* = 6.7 Hz, 1H), 3.60 (d, *J* = 10.0 Hz, 1H), 3.57 (m, 2H), 3.49 (m, 3H), 3.34 (s, 3H), 3.32 (d, *J* = 15.0 Hz, 1H), 3.30 (s, 3H), 3.27 (s, 3H), 2.99 (d, *J* = 15.0 Hz, 1H), 2.78 (d, *J* = 12.5 Hz, 1H), 2.55 (m, 1H), 2.45 (m, 2H), 2.30 (m, 5H), 2.09 (d, *J* = 13.0 Hz 1H), 2.04 (m, 1H), 1.99 (s, 3H), 1.90 (m, 4H), 1.79 (s, 3H), 1.75 (m, 1H), 1.55 (m, 1H), 1.36 (m, 3H), 1.09 (s, 9H), 1.04 (m, 1H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.89 (s, 9H), 0.76 (d, *J* = 6.5 Hz, 3H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (125 MHz) δ 165.6, 161.4, 159.3, 144.3, 142.4, 141.8, 137.9, 137.3, 136.2, 135.7, 134.2, 134.1, 133.9, 133.7, 132.4, 129.8, 128.1, 127.7, 125.5, 121.0, 119.3, 110.1, 106.3, 99.8, 89.3, 81.2, 79.5, 78.0, 73.6, 73.5, 72.1, 70.0, 69.1, 68.9, 67.2, 66.0, 56.6, 55.3, 55.6, 47.9, 41.4, 39.3, 39.1, 39.0, 38.9, 37.0, 35.6, 35.3, 34.4, 32.6, 31.8, 30.5, 30.3, 27.0, 25.8, 22.7, 21.1, 19.3, 18.2, 15.2, 14.2, 13.4, 13.4, 6.0, -4.5, -4.6; HRMS calc. for $C_{76}H_{105}N_2O_{13}Si_2Br$ $[M+Na]^+$ 1411.6236, found 1411.6245. Copies of ^1H NMR and ^{13}C NMR spectra of compound **27** are included below.



(2*Z*)-45,46-Dehydrobromo-amide (32).

To a solution of (2*Z*)-macrolide **16** (9.2 mg, 9.6 μmol) in CH_2Cl_2 (2.3 mL) was added TFA (0.23 mL). The solution was stirred for 30 min and the volatile components were removed under a stream of N_2. The residue was dried under vacuum for 1 h before an aqueous phosphate buffer (pH 5.7, 2.4 mL) was added. The mixture was stirred for 1 h, then extracted with diethyl ether (5 ✖ 4 mL). The combined extracts were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to give the crude ammonium salt. To a stirred solution of carboxylic acid **31**[1] (5.0 mg, 10 μmol) in CH_2Cl_2 (2.4 mL) was added PyAOP (5.1 mg, 10 μmol) and *i*-

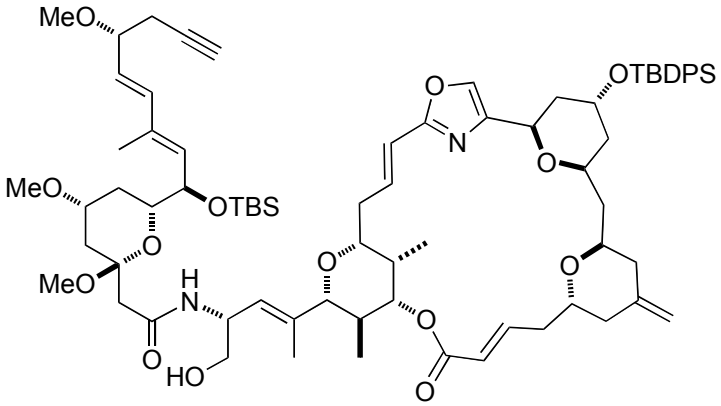
Pr_2NEt (51 μL, 0.32 mmol). The solution was stirred for 1 min before a solution of the crude ammonium salt of the macrolide in CH_2Cl_2 (2.3 mL) was added. After stirring for 9 h, the reaction mixture was diluted with diethyl ether (5 mL) and washed with saturated aqueous $NaHCO_3$ (10 mL). The aqueous phase was extracted with diethyl ether (5 × 5 mL), and the combined organic phase was dried over Na_2SO_4, filtered and concentrated. Flash column chromatography (hexanes–ethyl acetate, 1:1 to 1:2) gave **32** (12.1 mg, 9.1 μmol, 92%) as a white film: R_f 0.3 (hexanes–ethyl acetate, 1:2); $[\alpha]_D^{23}$ +9.3 (c 0.22, $CHCl_3$); IR 3374, 3311, 3070, 2927, 2856, 1717, 1653, 1521, 1461, 1428, 1360, 1302, 1248, 1188, 1158, 1092, 1052, 971, 938, 913, 887, 846, 776, 740, 702 cm^{-1}; ^{1}HNMR (500 MHz) δ 7.64 (t, J = 7.0 Hz, 4H), 7.40 (m, 7H), 6.84 (d, J = 8.0 Hz, 1H), 6.70 (ddd, J = 16.0, 10.0, 6.0 Hz, 1H), 6.28 (dd, J = 12.0, 16.0 Hz, 1H), 5.92 (s, 2H), 5.62 (dd, J = 15.7, 7.5 Hz, 1H), 5.40 (dd, J = 21.5, 9.0 Hz, 1H), 5.02 (m, 2H), 4.95 (d, J = 11.5 Hz, 1H), 4.77 (m, 1H), 4.64 (s, 1H), 4.50 (dd, J = 9.5, 7.0 Hz, 1H), 4.47 (dd, J = 11.5, 4.5 Hz, 1H), 4.33 (app s, 1H), 3.80 (dd, J = 13.0, 6.0 Hz, 1H), 3.73 (m, 1H), 3.65 (m, 2H), 3.60 (m, 1H), 3.50 (m, 1H), 3.43 (d, J = 10.0 Hz, 1H), 3.30 (s, 3H), 3.29 (s, 3H), 3.20 (s, 3H), 2.77 (m, 1H), 2.74 (m 1H), 2.52 (m, 1H), 2.50 (d, J = 14.5 Hz, 1H), 2.42 (m, 2H), 2.29 (m, 5H), 2.08 (d, J = 15.0 Hz, 1H), 1.91 (m, 5H), 1.80 (d, J = 1.0 Hz, 3H), 1.79 (d, J = 1.0 Hz, 3H), 1.74 (m, 1H), 1.55 (d, J = 14.0 Hz, 1H), 1.36 (m, 3H), 1.12 (m, 1H), 0.18 (s, 9H), 0.95 (d, J = 7.0 Hz, 3H), 0.88 (s, 9H), 0.72 (d, J = 6.5 Hz, 3H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}CNMR (75 MHz) δ 168.8, 165.5, 161.2, 144.3, 142.1, 141.6, 137.8, 136.9, 135.6, 134.1, 133.9, 133.6, 132.1, 129.6, 127.6, 126.1, 125.3, 120.9, 119.1, 109.9, 99.4, 88.8, 80.1, 79.3, 77.1, 73.7, 73.3, 73.0, 71.9, 69.9, 68.9, 68.8, 67.1, 65.8, 65.4, 56.5, 55.4, 49.1, 47.5, 43.8, 41.2, 39.2, 38.9, 37.8, 36.9, 35.1, 34.2, 31.1, 30.2, 29.6, 26.9, 25.7, 25.5, 22.6, 21.1, 19.2, 18.1, 13.3, 13.2, 11.9, 5.9, -4.5, -4.7; HRMS calcd for $C_{76}H_{108}N_2O_{14}Si_2$ $[M+K]^+$ 1367.6971, found 1367.6978. Copies of ^{1}H NMR and ^{13}C NMR spectra of compound **32** are included below.



(2*Z*)-45,46-Dehydrobromo-bisoxazole (33).

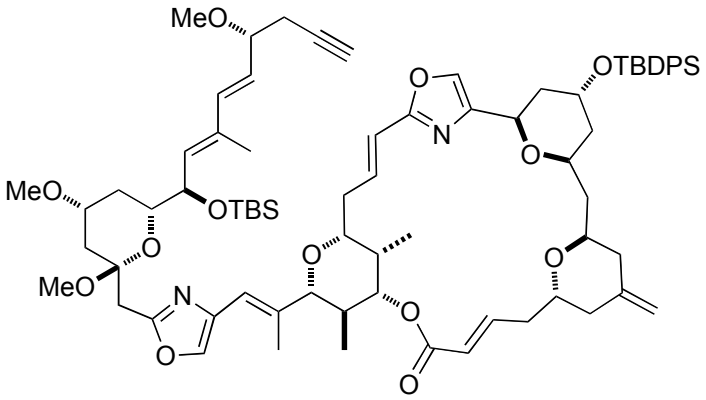
$NaHCO_3$ (400 mg, 4.8 mmol), Dess-Martin periodinane[2] (381 mg, 0.9 mmol), and *t*-butanol (83 μL, 0.9 mmol) were stirred in CH_2Cl_2 (12 mL) for 5 min then cooled to 0 °C. A pre-cooled solution of amide **32** (19 mg, 14.1 μmol) in CH_2Cl_2 (0.55 mL) was added. After stirring for 45 min, one-half of CH_2Cl_2 was evaporated under a

stream of N_2 and the original volume was made up with diethyl ether. Suspension of the resulting mixture was accomplished with sonication. Flash column chromatography (diethyl ether) of the mixture, followed by concentration gave the aldehyde free of Dess-Martin periodinane derived impurities. The diethyl ether was removed under a stream of N_2, and the residual aldehyde was placed under high vacuum for 30 min. The aldehyde was then dissolved in CH_2Cl_2 (10 mL), and Ph_3P (50 mg, 0.19 mmol), *i*-Pr_2NEt (135 μL, 0.77 mmol) and $(BrCCl_2)_2$ (62 mg, 0.19 mmol) were sequentially added. The mixture was stirred for 9 h before additional *i*-Pr_2NEt (135 μL, 0.77 mmol) was then added. After 2 h, diethyl ether and saturated aqueous NH_4Cl were added. The separated aqueous phase was extracted with diethyl ether (3 × 5 mL). The combined organic phase was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (hexanes–ethyl acetate, 2:1) to give bisoxazole **33** (12.6 mg, 9.6 μmol, 71% for two steps) as a white film: R_f 0.4 (hexanes–ethyl acetate, 2:1); $[\alpha]_D^{23}$ +56.5 (c 0.17, $CHCl_3$); IR 3640, 3310, 3071, 3049, 2927, 2855, 2358, 2121, 1719, 1657, 1640, 1579, 1553, 1462, 1428, 1379, 1359, 1320, 1300, 1259, 1188, 1156, 1092, 1052, 938, 914, 887, 836, 813, 778, 739, 702, 665, 636, 609 cm^{-1}; ^{1}HNMR (500 MHz) δ 7.65 (t, J = 8.0 Hz, 4H), 7.55 (s, 1H), 7.40 (m, 7H), 6.72 (ddd, J = 16.0, 10.0, 6.5 Hz, 1H), 6.31 (d, J = 15.5 Hz, 1H), 6.28 (s, 1H), 5.92 (m, 2H), 5.60 (dd, J = 15.8, 7.7 Hz, 1H), 5.40 (d, J = 9.0 Hz, 1H), 5.04 (s, 2H), 4.91 (d, J = 12.0 Hz, 1H), 4.66 (s, 1H), 4.53 (dd, J = 11.3, 4.2 Hz, 1H), 4.43 (dd, J = 9.5, 7.0 Hz, 1H), 4.33 (m, 1H), 4.20 (m, 2H), 3.99 (m, 1H), 3.82 (dd, J = 14.0, 6.5 Hz, 1H), 3.60 (d, J = 10.0 Hz, 1H), 3.57 (m, 2H), 3.49 (m, 2H), 3.34 (s, 3H), 3.32 (s, 3H), 3.30 (s, 3H), 2.99 (d, J = 15.0 Hz, 1H), 2.78 (d, J = 12.5 Hz, 1H), 2.55 (m, 1H), 2.45 (m, 2H), 2.30 (m, 4H), 2.29 (m, 3H), 2.09 (d, J = 13.0 Hz, 1H), 2.04 (m, 1H), 1.99 (s, 3H), 1.90 (m, 4H), 1.79 (s, 3H), 1.75 (m, 1H), 1.6-1.5 (m, 2H), 1.36 (m, 3H), 0.19 (s, 9H), 0.99 (d, J = 7.0 Hz, 3H), 0.89 (s, 9H), 0.76 (d, J = 6.5 Hz, 3H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}CNMR (125 MHz) δ 165.6, 161.4, 159.3, 144.4, 142.2, 141.7, 137.6, 137.1, 136.3, 135.7, 134.2, 134.0, 133.9, 133.8, 132.5, 129.8, 127.7, 127.4, 125.5, 121.0, 119.4, 119.2, 110.2, 99.8, 89.3, 80.6, 80.3, 79.4, 78.0, 73.6, 73.5, 72.1, 71.7, 71.5, 71.4, 70.0, 69.1, 68.9, 67.2, 65.9, 56.6, 55.7, 47.9, 41.3, 39.3, 39.1, 38.9, 37.0, 35.6, 35.2, 34.4, 32.6, 31.8, 30.5, 30.3, 29.7, 27.0, 25.8, 25.7, 19.3, 18.2, 14.2, 13.5, 13.3, 6.0, -4.5, -4.6; HRMS calcd for $C_{76}H_{104}N_2O_{13}Si_2$ $[M+Na]^+$ 1331.6973, found 1331.6976. Copies of ^{1}H NMR and ^{13}C NMR spectra of compound **33** are included below.



(2*E*)-45,46-Dehydrobromo-amide (38).

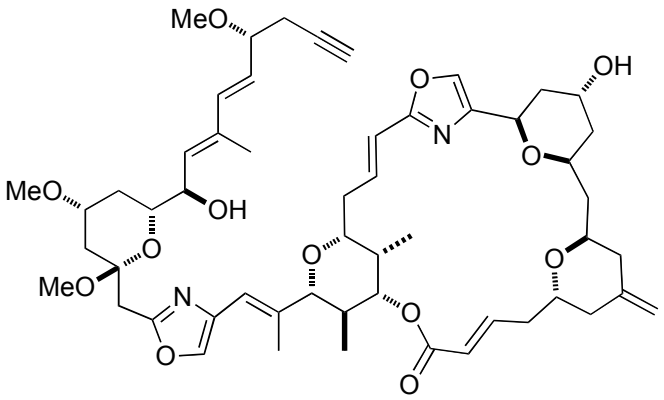
To a solution of (2*E*)-macrolide **17** (37 mg, 39 μmol) in CH_2Cl_2 (10.5 mL) was added TFA (1.0 mL). The solution was stirred for 40 min before the volatile components were removed under a stream of N_2. The residue was dried under vacuum for 1 h before an aqueous phosphate buffer (pH 5.7, 11 mL) was added. The mixture was stirred for 1 h, then extracted with diethyl ether (5 ✖ 10 mL). The combined extracts were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to give the crude ammonium salt. To a stirred solution of carboxylic acid **31**[1] (23 mg, 44 μmol) in CH_2Cl_2 (10.5 mL) was added PyAOP (24 mg, 229 μmol) and *i*-Pr_2NEt (230 μL, 1.3 mmol). The solution was stirred for 1 min before a solution of the crude ammonium salt of the macrolide CH_2Cl_2 (10.5 mL) was added. After stirring for 9 h, the reaction mixture was diluted with diethyl ether (20 mL) and washed with saturated aqueous $NaHCO_3$ (20 mL). The aqueous phase was extracted with diethyl ether (5 ✖ 20 mL), and the combined organic phase was dried over Na_2SO_4, filtered and concentrated. Flash column chromatography (hexanes–ethyl acetate, 1:1 to 1:2) gave **38** (52 mg, 37 μmol, 96%) as a white film: R_f 0.25 (hexanes–ethyl acetate, 1:2); $[\alpha]_D^{23}$ –45.5 (c 0.25, $CHCl_3$); IR 3374, 3311, 3071, 2930, 2856, 1709, 1654, 1526, 1461, 1427, 1379, 1359, 1324, 1308, 1248, 1153, 1089 cm^{-1}; ^{1}HNMR (500 MHz) δ 7.64 (t, J = 6.0 Hz, 4H), 7.42 (m, 7H), 6.84 (d, J = 8.0 Hz, 1H), 6.58 (ddd, J = 16.0, 10.0, 6.0 Hz, 1H), 6.26 (dd, J = 15.5, 5.0 Hz, 1H), 5.87 (d, J = 15.5 Hz, 1H), 5.60 (dd, J = 16.0, 7.5 Hz, 1H), 5.40 (dd, J = 19.5, 8.5 Hz, 1H), 5.02 (m, 1H), 4.92 (d, J = 11.5 Hz, 1H), 4.84-4.77 (m, 2H), 4.48 (dd, J = 8.5, 6.5 Hz, 1H), 4.31 (s, 1H), 4.16 (m, 1H), 3.85 (m, 1H), 3.80 (m, 1H), 3.70 (m, 1H), 3.62 (m, 2H), 3.60 (m, 1H), 3.50 (m, 1H), 3.46 (d, J = 6.5 Hz, 1H), 3.43 (d, J = 9.5 Hz, 1H), 3.31 (s, 3H), 3.28 (s, 3H), 3.18 (s, 3H), 2.71 (m, 1H), 2.70 (m 1H), 2.50-2.40 (m, 2H), 2.40-2.22 (m, 4H), 2.00-1.40 (m, 10H), 1.36 (d, J = 4.5 Hz, 3H), 1.12 (m, 1H), 0.18 (s, 9H), 0.95 (d, J = 7.0 Hz, 3H), 0.88 (s, 9H), 0.72 (d, J = 6.5 Hz, 3H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}CNMR (75 MHz) δ 168.9, 167.00, 161.1, 146.9, 142.3, 141.4, 137.9, 137.0, 135.5, 134.1, 133.8, 132.1, 129.7, 127.6, 126.0, 125.4, 122.8, 118.6, 111.1, 99.4, 88.9, 80.4, 80.1, 78.3, 74.6, 73.6, 73.0, 71.9, 70.4, 70.2, 70.0, 68.4, 66.0, 65.7, 65.5, 56.6, 56.1, 55.5, 49.1, 47.6, 43.7, 40.3, 38.9, 38.2, 37.8, 36.5, 34.2, 31.3, 30.2, 29.6, 26.9, 25.7, 25.5, 19.2, 18.1, 13.3, 13.2, 11.9, 5.8, -4.5, -4.7; HRMS calcd for $C_{76}H_{108}N_2O_{14}Si_2$ $[M+Na]^+$ 1351.7231, found 1351.7239. Copies of ^{1}H NMR and ^{13}C NMR spectra of compound **38** are included below.



(2*E*)- 45,46-Dehydrobromo-bisoxazole (39).

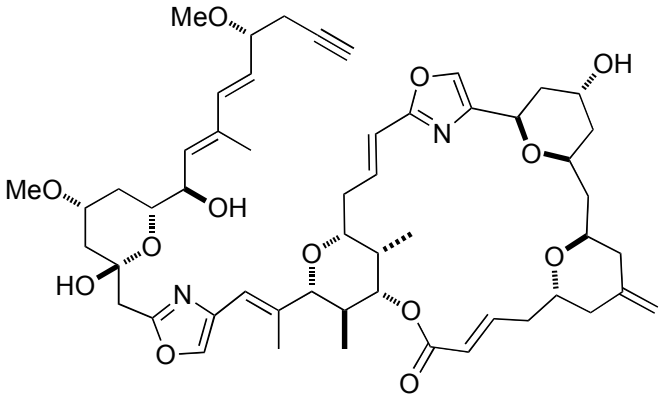
$NaHCO_3$ (800 mg, 9.5 mmol), Dess-Martin periodinane[2] (790 mg, 1.9 mmol), and *t*-butanol (173 μL, 1.9 mmol) were stirred in CH_2Cl_2 (12 mL) for 5 min then cooled to 0 °C. A pre-cooled solution of amide **38** (38 mg, 28 μmol) in CH_2Cl_2 (12 mL) was added. After stirring for 45 min, one-half of CH_2Cl_2 was evaporated under a stream of N_2 and the volume was made up with diethyl ether. The resulting mixture was briefly sonicated. Flash column chromatography (diethyl ether) of the mixture gave the aldehyde free of Dess-Martin periodinane derived impurities. The diethyl ether was removed under a stream of N_2, and the aldehyde was placed under high vacuum for 30 min. To this crude aldehyde in CH_2Cl_2 (21 mL) was added Ph_3P (102 mg, 125 μmol), *i*-Pr_2NEt (300 μL, 1.7 mmol) and $(BrCCl_2)_2$ (127.3 mg, 0.19 mmol) sequentially. The mixture was stirred for 9 h before additional *i*-Pr_2NEt (300 μL, 125 μmol) was added. After 2 h, the solution was diluted with diethyl ether (10 mL) and saturated aqueous NH_4Cl. The separated aqueous phase was extracted with diethyl ether (3 × 10 mL). The combined organic phase was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (hexanes–ethyl acetate, 2:1) to give bisoxazole **39** (25 mg, 19 μmol, 68% for two steps) as a white film: R_f 0.5 (hexanes–ethyl acetate, 2:1); $[\alpha]_D^{23}$ –11.4 (c 0.35, $CHCl_3$); IR 2934, 1717, 1654, 1640, 1463, 1357, 1098, 911, 839 cm^{-1}; ^{1}HNMR (500 MHz) δ 7.65 (t, J = 8.0 Hz, 4H), 7.55 (s, 1H), 7.40 (m, 7H), 6.72 (ddd, J = 16.0, 10.0, 6.5 Hz, 1H), 6.31 (d, J = 15.5 Hz, 1H), 6.28 (s, 1H), 5.92 (m, 2H), 5.46 (dd, J = 15.8, 7.7 Hz, 1H), 5.40 (d, J = 9.0 Hz, 1H), 5.04 (s, 2H), 4.91 (d, J = 12.0 Hz, 1H), 4.66 (s, 1H), 4.53 (dd, J = 11.3, 4.2 Hz, 1H), 4.43 (dd, J = 9.5, 7.0 Hz, 1H), 4.33 (m, 1H), 4.20 (m, 2H), 3.99 (m, 1H), 3.82 (dd, J = 14.0, 6.5 Hz, 1H), 3.60 (d, J = 10.0 Hz, 1H), 3.57 (m, 2H), 3.49 (m, 2H), 3.34 (s, 3H), 3.32 (s, 3H), 3.30 (s, 3H), 2.99 (d, J = 15.0 Hz, 1H), 2.78 (d, J = 12.5 Hz, 1H), 2.55 (m, 1H), 2.45 (m, 2H), 2.30 (m, 5H), 2.29 (m, 4H), 2.09 (d, J = 13.0 Hz, 1H), 2.04 (m, 1H), 1.99 (s, 3H), 1.90 (m, 4H), 1.79 (s, 3H), 1.75 (m, 1H), 1.6-1.5 (m, 2H), 1.36 (m, 3H), 0.19 (s, 9H), 0.99 (d, J = 7.0 Hz, 3H), 0.89 (s, 9H), 0.76 (d, J = 6.5 Hz, 3H), 0.07 (s, 3H), 0.03 (s, 3H); ^{13}CNMR (75 MHz) δ 166.9, 161.1, 159.1, 146.8, 142.3, 141.4, 137.7, 137.5, 137.0, 136.1, 135.5, 134.5, 134.0, 133.8, 133.7, 132.3, 129.7, 127.2, 125.4, 122.8, 119.2, 118.7, 110.0, 99.7, 89.3, 80.5, 80.2, 78.3, 76.7, 73.4, 73.3, 70.4, 69.9, 68.4, 66.0, 65.6, 56.5, 55.6, 47.9, 40.5, 40.3, 39.0, 38.9, 38.3, 37.5, 36.5, 35.5, 34.5, 34.3, 32.5, 32.0, 30.2,

29.6, 25.7, 25.6, 19.2, 18.1, 14.2, 13.4, 13.1, 5.9, -4.65, -4.71; HRMS calcd for $C_{76}H_{104}N_2O_{13}Si_2$ $[M+Na]^+$ 1331.6973, found 1331.6979. Copies of ^1H NMR and ^{13}C NMR spectra of compound **39** are included below.



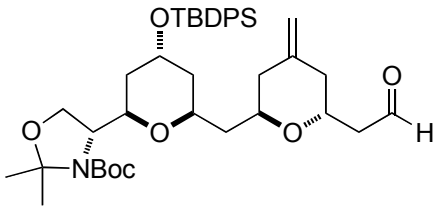
(2*E*)-33-*O*-Methyl-45,46-Dehydrobromo-phorboxazole A (40).

To bisoxazole **39** (0.7 mg, 0.5 μmol) in ethyl acetate (0.5 mL) was added TBAF (1.0 M in THF, 0.2 mL, 0.2 mmol). The mixture was stirred for 5 d then washed with saturated aqueous NH_4Cl (0.5 mL). The aqueous phase was extracted with ethyl acetate (5 × 1 mL), and the combined organic phase was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (EtOAc) to give **40** (0.4 mg, 0.4 μmol, 80%) as a white film: R_f 0.46 (ethyl acetate); $[\alpha]_D^{23}$ –31.7 (c 1.2, $CHCl_3$); IR 3447, 2929, 1643, 1456, 1371, 1180, 1156, 1092, 1040 cm^{-1}; ^1H NMR (500 MHz) δ 7.58 (s, 1H,), 7.43 (s, 1H), 6.61 (ddd, *J* = 16.5, 10.5, 5.0 Hz, 1H), 6.31 (d, *J* = 6.5 Hz, 1H), 6.28 (m, 2H), 5.64 (dd, *J* = 15.5, 7.5 Hz, 1H), 5.49 (d, *J* = 9.0 Hz, 1H), 4.76 (dd, *J* = 11.0, 3.5 Hz, 1H), 4.87 (d, *J* = 12.0 Hz, 1H), 4.78 (d, *J* = 12.0 Hz, 1H), 4.40 (m, 2H), 4.07 (d, *J* = 9.5 Hz, 1H), 3.95 (t, *J* = 11.0 Hz, 1H), 3.80 (m, 1H), 3.74 (m, 1H), 3.67 (dd, *J* = 11.5, 5.4 Hz, 1H), 3.60 (app d, *J* = 10.0 Hz, 2H), 3.55-3.49 (m, 3H), 3.36 (s, 3H), 3.31 (s, 3H), 3.25 (d, *J* = 11.5 Hz, 1H), 3.10 (d, *J* = 15.0 Hz, 1H), 2.78 (m, 1H), 2.65 (m, 1H), 2.45 (m, 1H), 2.35 (app q, *J* = 10.5 Hz, 1H), 2.25 (dd, *J* = 12.5, 4.0 Hz, 1H), 2.04 (bd, *J* = 13.0 Hz, 1H), 2.01 (t, *J* = 3.0 Hz, 1H), 1.98 (s, 3H), 1.90 (m, 2H), 1.79 (s, 3H), 1.42 (ddd, *J* = 13.0, 10.0, 3.1 Hz, 1H), 1.37 (q, *J* = 7.5 Hz, 1H), 1.11 (m, 1H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz) δ 161.0, 158.8, 142.0, 140.4, 137.7, 137.2, 137.0, 136.8, 136.3, 134.3, 134.1, 129.8, 128.2, 119.3, 118.9, 11.5, 99.9, 89.1, 80.4, 80.1, 79.4, 77.1, 75.0, 73.0, 72.8, 71.0, 69.9, 69.1, 67.4, 65.5, 64.3, 64.0, 57.7, 53.3, 49.4, 48.1, 43.5, 39.5, 39.0, 36.5, 35.5, 34.8, 34.6, 34.4, 32.7, 32.2, 29.6, 25.6, 20.6, 14.1, 13.9, 13.4, 13.1, 5.8; HRMS calc. for $C_{54}H_{72}N_2O_{13}$ $[M+Na]^+$ 979.4927, found 979.4933. Copies of ^1H NMR and ^{13}C NMR spectra of compound **40** are included below.



(2*E*)-45,46-Dehydrobromo-phorboxazole A (41).

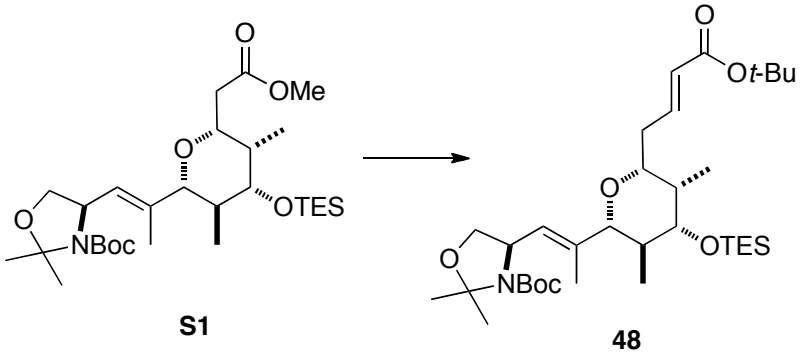
To **40** (2.4 mg, 2.4 μmol) in THF (3.0 mL) was added 6% aqueous HCl (0.7 mL). The mixture was stirred for 30 h, and washed with saturated aqueous $NaHCO_3$ (5.0 mL). The aqueous phase was extracted with ethyl acetate (5 × 2 mL), and the combined organic phase was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (ethyl acetate) to give **41** (1.6 mg, 1.6 μmol, 67%) as a white film: R_f 0.2 (ethyl acetate); $[\alpha]_D^{23}$ –10.0 (c 0.7, $CHCl_3$); IR 3414, 2961, 1744, 1650, 1411, 1357, 1323, 1260, 1188, 1091, 1015, 903, 871, 800 cm^{-1}; ^1H NMR (800 MHz, $CHCl_3$) δ 7.58 (m, 1H,), 7.45 (s, 1H), 6.63 (ddd, *J* = 16.5, 10.5, 5.0 Hz, 1H), 6.31 (d, *J* = 6.5 Hz, 1H), 6.28 (s, 2H), 5.64 (dd, *J* = 15.5, 7.5 Hz, 1H), 5.37 (d, *J* = 9.0 Hz, 1H), 5.31 (d, *J* = 2.0 Hz, 1H), 5.00 (dd, *J* = 10.5, 4.0 Hz, 1H), 4.88 (d, *J* = 12.0 Hz, 1H), 4.78 (dd, *J* = 12.0, 2.0 Hz, 1H), 4.40 (m, 2H), 4.32 (t, *J* = 8.0 Hz, 1H), 4.07 (t, *J* = 10.5 Hz, 1H), 3.95 (t, *J* = 11.0 Hz, 1H), 3.80-3.74 (m, 5H), 3.67 (dd, *J* = 11.5, 5.5 Hz, 4H), 3.60 (d, *J* = 10.0 Hz, 1H), 3.55 (d, *J* = 2.0 Hz, 1H), 3.52 (d, *J* = 1.5 Hz, 1H), 3.33 (s, 3H), 3.32 (s, 3H), 3.15 (d, *J* = 15.5 Hz, 1H), 3.10 (d, *J* = 15.5 Hz, 1H), 2.65 (m, 1H), 2.45 (m, 5H), 2.35 (m, 4H), 2.25 (dd, *J* = 12.5, 4.0 Hz 1H), 2.04 (bd, *J* = 13.0 Hz, 1H), 2.00 (t, *J* = 3.0 Hz, 1H), 1.98 (s, 3H), 1.90 (m, 2H), 1.79 (s, 3H), 1.42 (ddd, *J* = 13.0, 10.0, 3.1 Hz, 1H), 1.13 (q, *J* = 7.5 Hz, 1H), 1.11 (m, 1H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 6.5 Hz, 3H); HRMS calc. for $C_{54}H_{72}N_2O_{13}$ $[M+Na]^+$ 965.4771, found 965.4763; A copy of ^1H NMR spectrum of **41** is included below.



Aldehyde 52.

Alcohol **51** (100 mg, 144 μmol) was dissolved in CH_2Cl_2 (2.8 mL) and the solution was cooled to 0 °C. $NaHCO_3$ (89 mg, 1.0 mmol) and Dess-Martin periodinane (214 mg, 0.5 mmol) were added. The cold bath was removed and mixture was stirred for 20 min. Then the mixture was filtered through silica gel, eluted with hexanes–ethyl acetate (4:1), and the eluent was concentrated to give **52** (99 mg, 0.14 mmol, 99%) as a colorless

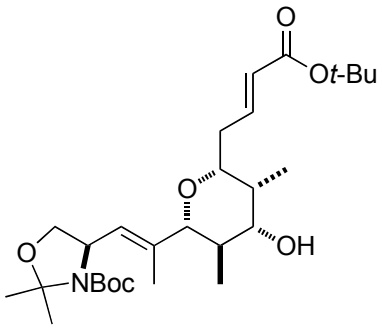
oil: R_f 0.60 (hexanes–ethyl acetate, 7:3); $[\alpha]_D^{23}$ –0.3 (*c* 4.43, $CHCl_3$); IR 3071, 2934, 2859, 1727, 1671, 1386, 1366, 1256, 1105, 1064 cm^{-1}; ^1H NMR (500 MHz, a mixture of carbamate rotamers) δ 9.75 (s, 1H), 7.63 (m, 4H), 7.65 (m, 4H), 7.38 (m, 6H), 4.82 (s, 1H), 4.81 (s, 1H), 4.44-4.37 (m, 1H), 4.32 (d, *J* = 11.0 Hz, 1H), 4.26 (d, *J* = 13.0 Hz, 1H), 4.10-3.95 (m, 4H), 3.86 (dd, *J* = 9.0, 7.0 Hz, 1H), 2.64 (dt, *J* = 15.0, 7.5 Hz, 1H), 2.53 (m, 1H), 2.40 (m, 2H), 2.05 (m, 2H), 1.81 (ddd, *J* = 14.5, 7.5, 6.5 Hz, 0.5H), 1.74 (ddd, *J* = 13.5, 7.5, 6.5 Hz, 0.5H), 1.59-1.42 (m, 17H), 1.29 (m, 3H), 1.07 (d, *J* = 4.0 Hz, 9H); ^{13}C NMR (125 MHz, a mixture of carbamate rotamers) δ 201.0, 200.7, 152.5, 152.4, 141.0, 135.8, 135.7, 135.6, 134.4, 134.0, 133.8, 129.8, 129.7, 129.6, 127.8, 127.7, 127.6, 112.7, 111.2, 11.1, 93.9, 93.4, 77.4, 77.1, 76.8, 71.0, 70.0, 69.5, 69.2, 69.0, 67.4, 67.3, 65.9, 63.6, 63.3, 59.4, 47.9, 39.7, 39.6, 39.2, 39.0, 38.7, 38.6, 32.7, 32.4, 29.7, 28.4, 27.0, 26.7, 25.9, 23.9, 22.5, 19.4, 19.3; HRMS calc. for $C_{40}H_{57}NO_7Si$ $[M+Na]^+$ 714.3802, found 714.3816. Copies of ^1H NMR and ^{13}C NMR spectra of compound **52** are included below.



***t*-Butyl ester 48**

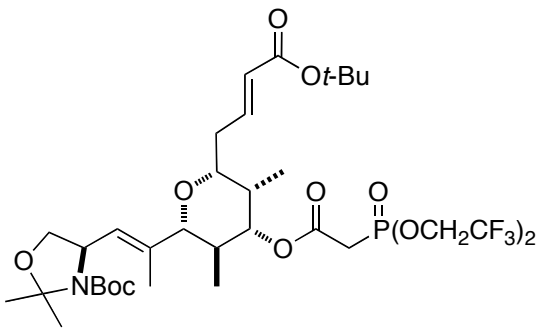
To a solution of ester **S1**[1] (445 mg, 801 μmol) in CH_2Cl_2 (4 mL) at –78 °C was added diisobutylaluminum hydride (150 μL, 840 μmol) dropwise. The resulting solution was allowed to stir for 5 h at –78 °C, before methanol (0.1 mL) was slowly added, followed by 10% aqueous HCl (5 mL) at –78 °C. Upon warming to rt, the aqueous layer was separated and extracted by diethyl ether (3 × 10 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated by rotary evaporation to give the crude aldehyde. To a portion of this aldehyde (69.2 mg, 131 μmol) in CH_3CN (0.65 mL) was added freshly prepared (*t*-butoxycarbonyl)methylene-triphenylphosphorane (86 mg, 228 μmol). After heating at 60 °C for 14 h, the reaction mixture was cooled to rt, diluted with diethyl ether (10 mL) and washed with saturated aqueous NH_4Cl (10 mL). The aqueous phase was extracted with diethyl ether (3 × 10 mL), and the combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The residue was subjected to flash column chromatography (hexanes–ethyl acetate, 5:1) to give **48** (55 mg, 98 μmol, 75%) as a colorless oil: R_f 0.4 (hexanes–ethyl acetate, 5:1); $[\alpha]_D^{23}$ +10.4 (*c* 2.8, $CHCl_3$); IR 2976, 2961, 2875, 1698, 1653, 1457, 1385, 1365, 1250, 1155, 1105, 1076 cm^{-1}; ^1H NMR (300 MHz, a mixture of carbamate rotamers) δ 6.84 (ddd, *J* = 13.8, 8.1, 6.3 Hz, 1H), 5.75 (d, *J* = 15.6 Hz, 1H), 5.33 (m, 1H), 4.55 (m, 1H), 3.99 (app t, *J* = 8.1 Hz, 1H), 3.73 (dd, *J* = 8.7, 1.2 Hz 1H), 3.43-

3.34 (m, 3H), 3.24 (d, J = 10.2 Hz, 1H), 2.41 (ddd, J = 14.0, 7.0, 7.0 Hz, 1H), 2.20 (ddd, J = 14.0, 7.0, 7.0 Hz, 1H), 1.70-1.50 (m, 11H), 1.43 (s, 9H), 1.39 (s, 9H), 0.90 (m, 12H), 0.74 (m, 3H), 0.56 (q, J = 7.8 Hz, 6H); ^{13}C NMR (75 MHz, a mixture of carbamate rotamers) δ 165.7, 151.7, 145.4, 143.9, 129.0, 127.7, 124.6, 105.3, 93.8, 88.5, 79.9, 79.5, 76.9, 68.8, 68.0, 54.5, 39.0, 35.4, 34.0, 28.4, 28.1, 28.0, 6.8, 5.6, 4.9; HRMS calcd. for $C_{34}H_{61}NO_7Si$ $[M+Na]^+$ 646.4110; found 646.4116. Copies of ^{1}H NMR and ^{13}C NMR spectra of compound **48** are included below.



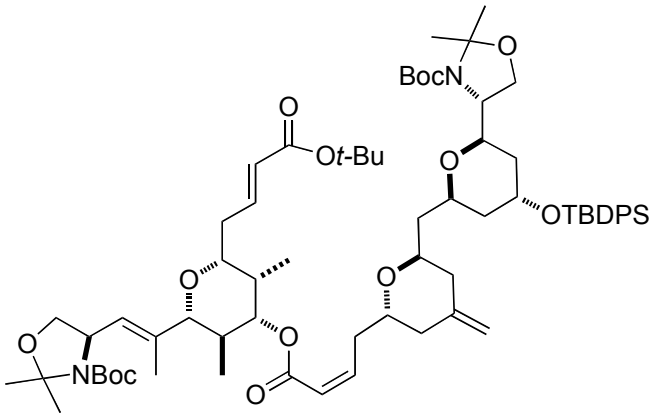
Alcohol 53.

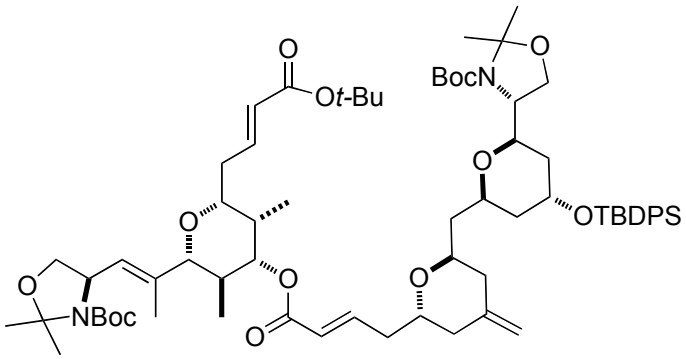
To a 0 °C solution of **48** (90 mg, 0.14 mmol) in THF (1 mL) was added TBAF (0.16 mL, 1M in THF). The solution was stirred at rt for 30 min then concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate, 3:1) to give **53** (71 mg, 0.14 mmol, 97%) as a colorless oil: R_f 0.32 (hexanes–ethyl acetate, 7:3); $[\alpha]_D^{23}$ +2.7 (*c* 5.85, $CHCl_3$); IR 3493, 2979, 2922, 2873, 1694, 1383, 1371, 1246, 1154, 1101, 1056 cm^{-1}; ^{1}H NMR (500 MHz, a mixture of carbamate rotamers) δ 6.76 (ddd, J = 15.5, 8.5, 6.0 Hz, 1H), 5.79 (d, J = 15.5 Hz, 1H), 5.38-5.31 (m, 1H), 4.62-4.56 (m, 1H), 4.03 (m, 1H), 3.74 (d, J = 8.5 Hz, 1H), 3.50 (dt, J = 7.0, 2.0 Hz, 1H), 3.43 (m, 1H), 3.30 (d, J = 10.5 Hz, 1H), 2.44 (ddd, J = 15.0, 7.0, 6.0 Hz, 1H), 2.28 (ddd, J = 15.0, 8.5, 7.0 Hz, 1H), 1.85 (dq, J = 5.0, 2.0 Hz, 1H), 1.74 (m, 1H), 1.66 -1.41 (m, 27H), 0.92 (d, J = 7.0 Hz, 3H), 0.84-0.79 (m, 3H); ^{13}C NMR (125 MHz, a mixture of carbamate rotamers) δ 165.8, 151.9, 143.7, 135.9, 134.3, 129.3, 128.0, 124.8, 93.9, 93.2, 88.9, 88.4, 80.3, 79.7, 76.9, 76.5, 68.9, 68.0, 54.6, 38.0, 35.4, 33.7, 28.5, 28.3, 28.2, 28.1, 28.0, 27.6, 26.8, 25.1, 23.6, 13.7, 12.8, 11.6, 11.2, 5.4; HRMS calc. for $C_{28}H_{47}NO_7$ $[M+Na]^+$ 532.3250, found 532.3255. Copies of ^{1}H NMR and ^{13}C NMR spectra of **53** are included below.



Phosphonate 54.

To a solution of alcohol **53** (71 mg, 0.14 mmol) in CH_2Cl_2 (1.4 mL) was added bis(2,2,2-trifluoroethoxy)phosphono-acetic acid[3] (128 mg, 420 μmol) followed by EDCI·HCl (81 mg, 0.42 mmol) and HOBt (6 mg, 0.4 mmol). The mixture was stirred at rt for 20 min then chromatographed on silica gel (hexanes–ethyl acetate, 3:1) to give **54** (105 mg, 132 μmol, 94%) as a colorless oil: R_f 0.29 (hexanes–ethyl acetate, 7:3); $[\alpha]_D^{23}$ +3.8 (*c* 2.92, $CHCl_3$); IR 2979, 2937, 1733, 1700, 1394, 1367, 1299, 1266, 1172, 1102, 1074 cm^{-1}; ^1H NMR (500 MHz, a mixture of carbamate rotamers) δ 6.76 (ddd, *J* = 15.5, 8.5, 6.0 Hz, 1H), 5.80 (d, *J* = 15.5 Hz, 1H), 5.42-5.36 (m, 1H), 4.75 (dd, *J* = 11.0, 4.0 Hz, 1H), 4.62-4.59 (m, 1H), 4.46 (dq, *J* = 8.0, 1.5 Hz, 4H), 4.06 (m, 1H), 3.76 (d, *J* = 8.5 Hz, 1H), 3.55 (dt, *J* = 7.0, 2.0 Hz, 1H), 3.39 (d, *J* = 10.5 Hz, 1H), 3.21 (d, $J_{P\text{-}H}$ = 21.5 Hz, 2H), 2.45 (ddd, *J* = 15.0, 7.0, 6.0 Hz, 1H), 2.24 (ddd, *J* = 15.0, 8.5, 7.0 Hz, 1H), 2.05 (m, 1H), 1.91 (m, 1H), 1.77-1.40 (m, 27H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.77-0.71 (m, 3H); ^{13}C NMR (125 MHz, a mixture of carbamate rotamers) δ 165.7, 164.0, 151.8, 143.0, 135.2, 133.5, 130.2, 128.6, 125.7, 125.6, 125.2, 123.5, 123.4, 121.3, 121.2, 119.1, 119.0, 112.7, 94.0, 93.1, 88.8, 88.1, 80.7, 80.3, 79.7, 78.8, 78.7, 76.4, 68.8, 67.9, 62.4, 54.6, 35.3, 34.6, 33.5, 31.4, 29.7, 28.5, 28.3, 28.1, 28.0, 27.5, 26.8, 25.1, 24.7, 23.5, 13.3, 12.7, 12.6, 11.5, 11.1, 6.0; HRMS calc. for $C_{34}H_{52}F_6NO_{11}P$ $[M+Na]^+$ 818.3080, found 818.3073. Copies of ^1H NMR and ^{13}C NMR spectra of **54** are included below.





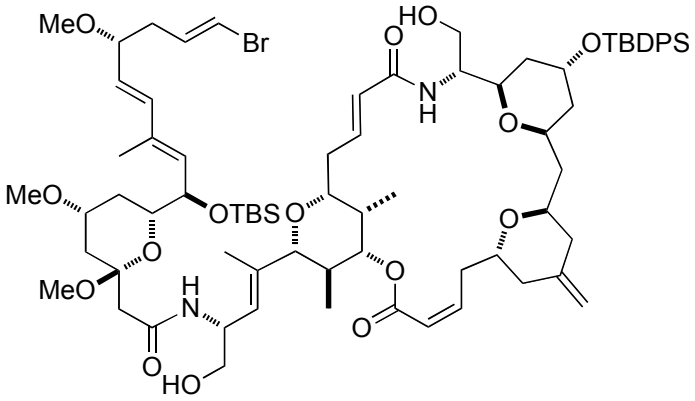
Acrylate (2*Z*)-47 and (2*E*)-47.

To a solution of 18-crown-6 (391 mg, 1.48 mmol) in toluene (1.5 mL) was added K_2CO_3 (102 mg, 738 μmol). The mixture was stirred for 10 h before being cooled to –40 °C. A solution of aldehyde **52** (98 mg, 0.12 mmol) and phosphonate **54** (85 mg, 0.12 mmol) in toluene (0.5 mL) was added. The resultant mixture was stirred at -40 °C for 2 h, then subjected directly to silica gel chromatography (hexanes–ethyl acetate, 3:1) to give a mixture of (2*Z*)-**47** and (2*E*)-**47** (2*Z* : 2*E* ≈ 3 : 1, as assayed by ^{1}H NMR spectroscopy, 140 mg, 114 μmol, 93%). Further flash chromatography provided (2*Z*)-**47** (98 mg, 80 μmol, 65%) separated from (2*E*)-**8**.

Analytical data for (2*Z*)-**47**: R_f 0.61 (hexanes–ethyl acetate, 7:3); $[\alpha]_D^{23}$ –4.8 (*c* 2.36, $CHCl_3$); IR 3074, 3048, 2979, 2934, 2892, 2858, 1700, 1390, 13657, 1255, 1160, 1104, 1063 cm^{-1}; ^{1}H NMR (500 MHz, a mixture of carbamate rotamers) δ 7.63 (m, 4H), 7.35 (m, 6H), 6.77 (ddd, *J* = 12.0, 8.0, 7.0 Hz, 1H), 6.38 (m, 1H), 5.79 (m, 2H), 4.78 (s, 1H), 4.75 (s, 1H), 4.71 (dd, *J* = 11.0, 4.5 Hz, 1H), 4.63-4.57 (m, 1H), 4.43 (d, *J* = 9.0 Hz, 0.5H), 4.32 (d, *J* = 10.5 Hz, 0.5H), 4.25 (m, 1H), 4.05 (m, 2H), 3.97 (t, *J* = 9.5 Hz, 1H), 3.94 (m, 1H), 3.88 (m, 1H), 3.84 (dd, *J* = 9.5, 6.5 Hz, 1H), 3.76 (d, *J* = 8.5 Hz, 1H), 3.58 (t, *J* = 6.0 Hz, 1H), 3.40 (d, *J* = 10.5 Hz, 1H), 2.95 (m, 1H), 2.81 (m, 1H), 2.45 (m, 1H), 2.40 (dd, *J* = 13.0, 3.5 Hz, 1H), 2.33 (appt, *J* = 13.0 Hz, 1H), 2.25 (m, 1H), 2.06 (m, 2H), 1.89 (m, 1H), 1.84 (m, 1H), 1.77-1.41 (m, 47H), 1.32-1.25 (m, 3H), 1.07 (d, *J* = 5.5 Hz, 9H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.73-0.68 (m, 3H); ^{13}C NMR (125 MHz, a mixture of carbamate rotamers) δ 165.8, 152.4, 151.8, 147.5, 143.4, 141.7, 135.7, 135.6, 134.4, 134.0, 133.7, 129.7, 129.5, 128.3, 127.7, 127.6, 125.1, 120.6, 112.4, 110.6, 93.9, 93.4, 89.0, 88.4, 80.3, 80.1, 79.7, 78.0, 76.6, 71.3, 70.9, 69.9, 69.5, 69.3, 69.1, 68.9, 68.0, 67.1, 65.9, 63.5, 63.3, 59.4, 54.6, 40.0, 39.8, 39.2, 38.9, 35.4, 33.9, 33.5, 32.7, 32.3, 31.7, 31.5, 30.3, 29.7, 28.6, 28.4, 28.2, 27.6, 27.0, 26.7, 25.9, 25.1, 24.7, 23.9, 23.6, 22.7, 22.4, 19.4, 15.3, 14.1, 13.5, 12.8, 11.7, 11.2, 6.3; HRMS calc. for $C_{70}H_{104}N_2O_{14}SiNa^+$ $[M+Na]^+$ 1247.7155, found 1247.7152. Copies of ^{1}H NMR and ^{13}C NMR spectra of (2*Z*)-**47** are included below.

Analytical data for (2*E*)-**47**: R_f 0.61 (hexanes–ethyl acetate, 7:3); $[\alpha]_D^{23}$ +1.89 (*c* 3.91, $CHCl_3$); ^{1}H NMR (500 MHz, a mixture of carbamate rotamers) δ 7.63 (m, 4H), 7.35 (m, 6H), 6.93 (m, 1H), 6.77 (ddd, *J* = 15.0, 8.0, 6.0

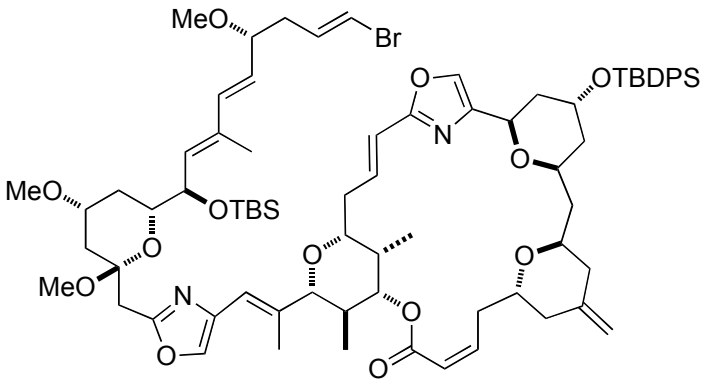
Hz, 1H), 5.86 (d, J = 15.5 Hz, 1H), 5.78 (d, J = 15.5 Hz, 1H), 5.42-5.35 (m, 1H), 4.87 (s, 1H), 4.78 (app d, J = 6.5 Hz, 1H), 4.73 (dd, J = 10.5, 3.5 Hz, 1H), 4.63-4.58 (m, 1H), 4.44 (d, J = 9.0 Hz, 0.5H), 4.32 (d, J = 10.5 Hz, 0.5H), 4.25 (d, J = 15.5 Hz, 1H), 4.05 (m, 4H), 4.00 (d, J = 15.5 Hz, 1H), 3.95 (t, J = 5.0 Hz, 0.5H), 3.90 (app q, J = 4.0 Hz, 0.5H), 3.85 (dd, J = 9.0, 6.5 Hz, 1H), 3.77 (d, J = 8.5 Hz, 1H), 3.60 (t, J = 5.5 Hz, 1H), 3.41 (d, J = 10.5 Hz, 1H), 2.43-2.39 (m, 4H), 2.33 (dq, J = 14.0, 2.5 Hz, 1H), 2.25 (m, 1H), 2.08-2.02 (m, 3H), 1.92 (m, 1H), 1.78-1.70 (m, 4H), 1.62-1.20 (m, 44H), 1.08 (d, J = 6.5 Hz, 9H), 0.93 (d, J = 7.0 Hz, 3H), 0.75-0.70 (m, 3H); ^{13}C NMR (125 MHz, a mixture of carbamate rotamers) δ 165.8, 152.4, 141.5, 135.8, 135.7, 135.6, 134.0, 129.8, 129.7, 127.6, 127.7, 127.6, 125.1, 93.9, 93.4, 80.3, 80.1, 79.8, 79.7, 78.3, 77.3, 76.6, 71.0, 70.8, 69.3, 68.9, 65.9, 63.5, 59.4, 54.7, 39.2, 38.9, 38.5, 36.7, 35.4, 35.3, 32.4, 31.6, 30.3, 29.7, 28.4, 28.2, 28.1, 27.0, 26.7, 26.9, 23.9, 22.7, 22.4, 19.4, 19.3, 14.1, 6.2; HRMS calc. for $C_{70}H_{104}N_2O_{14}SiNa^+$ $[M+Na]^+$ 1247.7155, found 1247.7152. Copies of ^{1}H NMR and ^{13}C NMR spectra of (2*E*)-**47** are included below.



Bisamide 44.

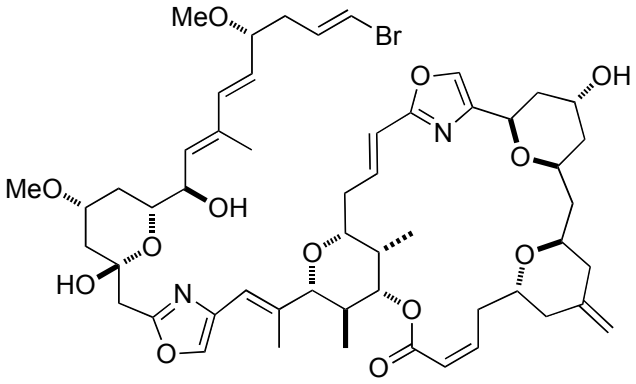
To a solution of (2*Z*)-**47** (38 mg, 31 μmol) in CH_2Cl_2 (2.5 mL) under argon was added freshly distilled trifluoroacetic acid (TFA, 2.5 mL). The solution was stirred for 50 min before the TFA and CH_2Cl_2 were removed under a gentle flow of nitrogen gas. The residue was further concentrated under high vacuum for 10 min and then stirred in a mixture of pH 5.7 aqueous phosphate buffer and $CHCl_3$ for 50 min. The separated aqueous phase was extracted with $CHCl_3$. The combined organic phase was dried over Na_2SO_4, concentrated, and further dried under high vacuum for 12 h to give **46** as a solid white bis-ammonium salt. This solid was dissolved in DMF (33 mL) and *i*-Pr_2NEt (0.3 mL) with the aid of sonication. A solution of pentafluorophenol diphenylphosphinate (30 mg, 78 μmol) in DMF (1 mL) was added over 1 h. After stirring for an additional 3 h, additional pentafluorophenol diphenylphosphinate (6 mg, 16 μmol) in DMF (1 mL) was added over 0.5 h. The mixture was stirred for an additional 3 h to completely generate lactam-lactone **49** *in situ* (monitored by ESI-TOF-HRMS analysis). In a separate vial, carboxylic acid **7**[1] (18 mg, 31 μmol) was dissolved in DMF (2 mL) and *i*-Pr_2NEt (50 μL) before PyAOP (16 mg, 31 μmol) was added. The mixture was gently shaken for 1 min before being added to the mixture of *in situ* generated **46**. The resultant mixture was stirred for 10 min before

methanol (2 mL) was added and the mixture was concentrated by rotary evaporation under high vacuum. The residue was subjected to flash chromatography ($CHCl_3$–MeOH, 1:0 to 100:1 to 70:1 to 50:1 to 30:1) to give **44** (37.5 mg) accompanied by impurities: R_f 0.42 ($CHCl_3$–MeOH, 12:1); HRMS calc. for $C_{76}H_{113}BrN_2O_{15}Si_2$ $[M+Na]^+$ 1451.6755, found 1451.6751; A copy of the ^1H NMR spectrum of crude **44** is included below.



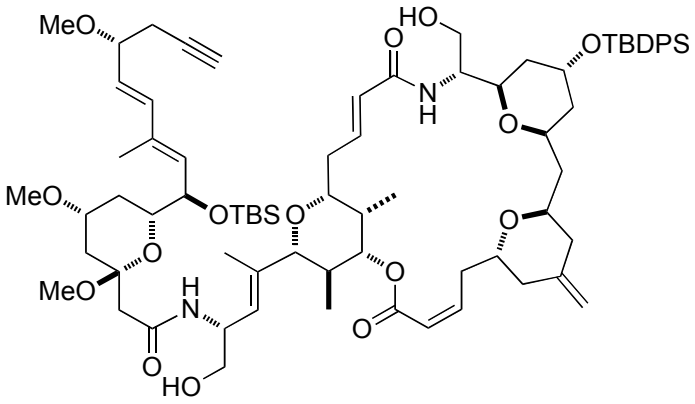
Bisoxazole 27 (Obtained via simultaneous oxazole formation).

To a mixture of $NaHCO_3$ (60 mg, 0.7 mmol), Dess-Martin periodinane[2] (54 mg, 1.3 mmol) and *t*-BuOH (60 μL) in CH_2Cl_2 (0.2 mL) was added a solution of crude bis-amido-diol **44** (5 mg) in CH_2Cl_2 (0.1 mL). The mixture was stirred for 20 min before a saturated aqueous solution of $Na_2S_2O_3$ and $NaHCO_3$, and diethyl ether, were added. The biphasic mixture was stirred vigorously for 5 min. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was dried over Na_2SO_4, filtered, concentrated and further dried under high vacuum for 30 min to give a crude bisamido-dialdehyde. This was dissolved in CH_2Cl_2 (4 mL) and to the solution were sequentially added Ph_3P (37 mg, 0.14 mmol), *i*-Pr_2NEt (200 μL) and $(BrCCl_2)_2$ (46 mg, 0.14 mmol). The mixture was stirred at rt for 4 h before the volume of CH_2Cl_2 was reduced to about 0.5 mL. CH_3CN (1.5 mL) and DBU (40 μL) were added sequentially. The mixture was stirred for an additional 1 h before saturated aqueous NH_4Cl and diethyl ether were added. The separated aqueous phase was extracted with additional diethyl ether. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate, 9:1 to 7:3) to give bisoxazole **27** (2.4 mg, 1.9 μmol, 45% from (2*Z*)-**47** as a white film. The analytical data of bisoxazole **27** thus prepared are identical to that obtained by sequential oxazole-formation process. A copy of ^1H NMR spectrum of compound **27** is included below.



Phorboxazole A (1)

To a solution of **27** (4.2 mg, 3.29 μmol) in ethyl acetate (0.1 mL) was added TBAF (0.5 mL, 1 M in THF). The solution was stirred for 20 h then washed with saturated aqueous NH_4Cl. The separated aqueous phase was extracted with ethyl acetate. The combined organic phase was dried over Na_2SO_4, filtered, concentrated, and purified by flash chromatography to give the 33-*O*-methyl-phorboxazole A (**28**, ca. 4 mg) as a colorless oil. This was dissolved in THF (1.7 mL) and aqueous HCl (0.72 M, 0.59 mL) was added. The mixture was stirred for 60 h, then neutralized by the addition of pH 7 aqueous phosphate buffer. The product was extracted with $CHCl_3$, dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography ($CHCl_3$–MeOH, 100:1 to 100:3 to 100:5) to give **1** (2.0 mg, 1.95 μmol, 59 %) as an amorphous solid. R_f 0.59 (HPTLC, $CHCl_3$–MeOH, 20:1), co-eluted with previously prepared phorboxzole A;[4] HRMS calc. for $C_{53}H_{71}BrN_2O_{13}$ $[M+Na]^+$ 1047.4017, found 1047.4013. Characterization data for **1** matched those previously reported.[5] A copy of ^1H NMR spectrum of **1** thus prepared is included below.

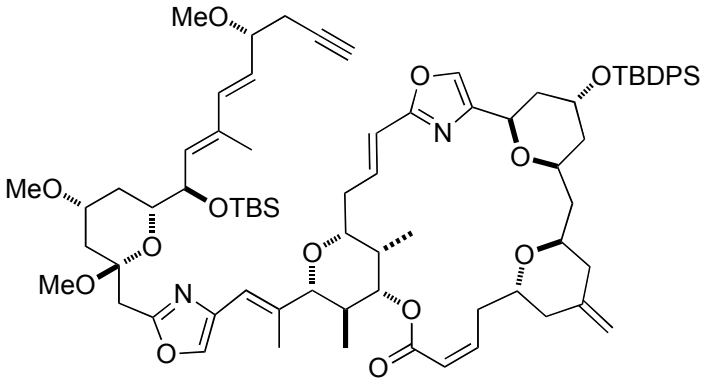


45,46-Dehydrobromo-bisamide 45.

To a stirred solution of (2*Z*)-**47** (60 mg, 49 μmol) in CH_2Cl_2 (4 mL) under argon was added freshly distilled TFA (4 mL). The resulting solution was stirred for 50 min before the TFA and CH_2Cl_2 were removed under a stream of nitrogen gas. The residue was further concentrated under high vacuum for 10 min and then stirred in a

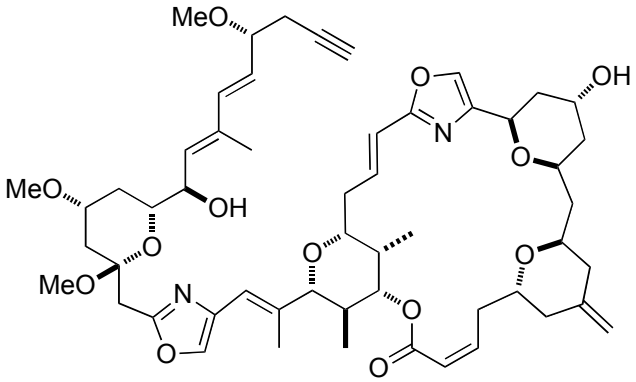
[5] (a) Searle, P. A.; Molinski, T. F. *J. Am. Chem. Soc.* **1995**, *117*, 8126-8131. (b) Searle, P. A.; Molinski, T. F.; Brzeinski, L. J.; Leahy, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 9422-9423. (c) Molinski, T. F. *Tetrahedron Lett.* **1996**, *37*, 7879-7980

mixture of aqueous pH 5.7 phosphate buffer and $CHCl_3$ for 50 min. The separated aqueous phase was extracted with $CHCl_3$ and the combined organic phase was dried over Na_2SO_4, filtered, concentrated, and further dried under high vacuum for 1 h to give a pale yellow solid (**46**). This solid was dissolved in DMF (50 mL) and *i*-Pr_2NEt (0.5 mL) with the aid of sonication. A solution of pentafluorophenyl diphenylphosphinate (47 mg, 0.12 mmol) in DMF (1 mL) was added over 1 h. After stirring for an additional 4 h, complete formation of macrolactam **49** was indicated by ESI-MS analysis. In a separate vial, the C31-C46 carboxylic acid **31**[1] (24 mg, 49 μmol) was dissolved in DMF (2 mL) and *i*-Pr_2NEt (0.1 mL) at rt. PyAOP (26 mg, 49 μmol) was added. The mixture was gently shaken for 1 min before being added to the solution of **49**. The resultant mixture was stirred for 20 min and then concentrated by rotary evaporation under high vacuum. The residue was purified by flash chromatography ($CHCl_3$–MeOH, 1:0 to 100:1 to 50:1 to 30:1) to give **45** (40 mg, 29 μmol, 60 %) as an amorphous solid: R_f 0.34 ($CHCl_3$–MeOH, 12:1); $[\alpha]_D^{23}$ +10.9 (*c* 1.41, $CHCl_3$); IR 3310, 3070, 2958, 2856, 1700, 1650, 1507, 1462, 1430, 1259 1102, 1027 cm^{-1}; ^1H NMR (500 MHz) δ 7.62 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 4H), 6.87 (d, *J* = 7.5 Hz, 1H), 6.62 (ddd, *J* = 15.5, 7.5, 5.0 Hz, 1H), 6.27 (d, *J* = 15.5 Hz, 1H), 6.20 (d, *J* = 8.5 Hz, 1H), 6.10 (dt, *J* = 11.5, 8.0 Hz, 1H), 5.89 (d, *J* = 16.0 Hz, 1H), 5.87 (d, *J* = 11.5 Hz, 1H), 5.61 (dd, *J* = 16.0, 7.5 Hz, 1H), 5.42 (d, *J* = 9.0 Hz, 1H), 5.37 (d, *J* = 8.5 Hz, 1H), 4.75 (m, 1H), 4.72 (m, 2 H), 4.53 (dd, *J* = 11.0, 4.0 Hz, 1H), 4.50 (dd, *J* = 9.0, 7.0 Hz, 1H), 4.26 (m, 1H), 4.24 (s, 1H), 4.08 (m, 2H), 3.93 (m, 1H), 3.90 (m, 1H), 3.86 (ddd, *J* = 15.5, 7.5, 5.0 Hz, 1H), 3.80 (ddd, *J* = 13.0, 6.0, 6.0 Hz, 1H), 3.74-3.50 (m, 6H), 3.45 (d, *J* = 10.0 Hz, 1H), 3.32 (s, 3H), 3.29 (s, 3H), 3.22 (t, *J* = 5.5 Hz, 1H), 3.19 (s, 3H), 2.96 (m, 1H), 2.75 (d, *J* = 15.0 Hz, 1H), 2.53-2.37 (m, 7H), 2.29 (dd, *J* = 13.0, 3.5 Hz, 1H), 2.21 (dd, *J* = 13.0, 4.5 Hz, 1H), 2.05-2.00 (m, 3H), 1.97 (dd, *J* = 11.0, 4.5 Hz, 1H), 1.94-1.90 (m, 2H), 1.80 (s, 3H), 1.77 (s, 3H), 1.77-1.75 (m, 1H), 1.62-1.59 (m, 1H), 1.43-1.35 (m, 4H), 1.25 (m, 2H), 1.11 (m, 1H), 1.08 (s, 9H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.87 (s, 9H), 0.72 (d, *J* = 6.5 Hz, 3H), 0.06 (s, 3H), 0.01 (s, 3H); ^{13}C NMR (75 MHz) δ 168.8, 166.3, 165.9, 143.6, 141.4, 138.3, 137.3, 137.0, 135.5, 134.1, 133.9, 133.5, 132.1, 129.7, 129.6, 127.5, 126.6, 125.9, 122.2, 109.9, 108.1, 106.5, 104.2, 99.3, 89.0, 80.4, 80.0, 79.5, 75.7, 74.1, 73.5, 73.0, 71.8, 71.3, 70.9, 70.0, 65.5, 64.9, 64.6, 56.4, 55.3, 53.7, 48.9, 47.5, 43.6, 40.2, 39.0, 38.1, 37.8, 37.7, 35.3, 33.5, 32.9, 32.4, 32.1, 30.9, 29.5, 26.8, 25.6, 25.4, 19.1, 18.0, 13.2, 11.7, 6.0, 0.8, -4.7, -4.9; HRMS calc. for $C_{76}H_{112}N_2O_{15}Si_2$ $[M+Na]^+$ 1371.7499, found 1371.7505; Copies of the ^1H NMR and ^{13}C NMR spectra of compound **45** are included below.



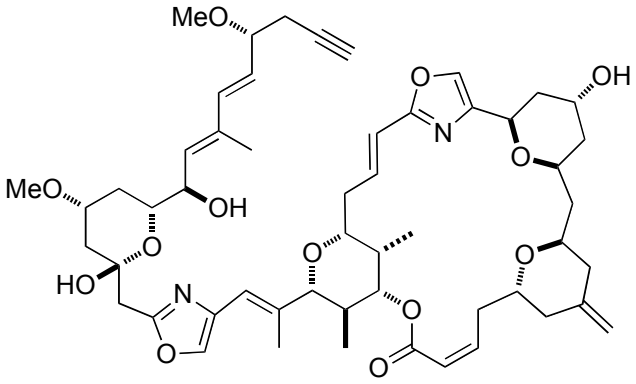
45,46-dehydrobromo-bisoxazole 33 (Obtained via simultaneous oxazole formation).

To a stirred mixture of $NaHCO_3$ (28 mg, 0.33 mmol), Dess-Martin periodinane[2] (25 mg, 60 μmol), *t*-BuOH (30 μL), and CH_2Cl_2 (0.2 mL) was added a solution of bisamido-diol **45** (4.1 mg, 3.0 μmol) in CH_2Cl_2 (0.1 mL). The resultant mixture was stirred for 25 min before saturated aqueous $Na_2S_2O_3$ and $NaHCO_3$, and diethyl ether were added. The biphasic mixture was stirred vigorously for 5 min. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was dried over Na_2SO_4, concentrated and dried further under high vacuum for 30 min to give crude the bisamido-dialdehyde. This was dissolved in CH_2Cl_2 (3 mL). Ph_3P (30 mg, 0.11 mmol), *i*-Pr_2NEt (80 μL) and $(BrCCl_2)_2$ (37 mg, 0.11 mmol) were added sequentially. The mixture was stirred for 4 h before the volume of CH_2Cl_2 was reduced to about 0.5 mL. CH_3CN (1.5 mL) and DBU (30 μL) were added sequentially. The mixture was stirred for an additional 1 h before saturated aqueous NH_4Cl and diethyl ether were added. The separated aqueous phase was extracted with diethyl ether. The combined organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography (hexanes–ethyl acetate, 9:1 to 7:3) to give bisoxazole **33** (3.1 mg, 2.4 μmol, 79%) as white film. The analytical data of bisoxazole **33** thus prepared are identical to those obtained by the sequential oxazole-formation process. Copies of the ^1H NMR and ^{13}C NMR spectra of compound **33** are included below.



33-*O*-Methyl-45,46-dehydrobromo-phorboxazole A (34).

To a solution of oxazole **33** (1.75 mg, 1.3 μmol) in ethyl acetate (1.4 mL) was added TBAF (1.0 M in THF, 0.55 mL, 0.55 μmol). The mixture was stirred for 5 d, then washed with saturated aqueous NH_4Cl (3.0 mL). The aqueous phase was extracted with ethyl acetate (5 × 5 mL), and the combined organic phase was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (ethyl acetate) to give **34** (1.1 mg, 1.1 μmol, 89%) as a white film: R_f 0.45 (ethyl acetate); $[\alpha]_D^{23}$ +12.0 (c 1.0, $CHCl_3$); IR 3444, 2930, 1645, 1456, 1378, 1188, 1156, 1089, 1040 cm^{-1}; ^1H NMR (500 MHz) δ 7.57 (s, 1H,), 7.42 (s, 1H), 6.69 (ddd, *J* = 16.0, 9.5, 6.5 Hz, 1H), 6.31 (dd, *J* = 16.0, 1.0 Hz, 1H), 6.27 (app s, 2H), 5.92 (m, 2H), 5.64 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.49 (d, *J* = 9.0 Hz, 1H), 4.99 (s, 1H), 4.74 (dd, *J* = 10.5, 3.0 Hz, 1H), 4.62 (s, 1H), 4.52 (dd, *J* = 11.0, 4.0 Hz, 1H), 4.40 (m, 1H), 4.39 (m, 2H), 4.17 (m, 1H), 4.07 (app t, *J* = 11.0 Hz, 1H), 3.99 (m, 1H), 3.80 (ddd, *J* = 7.0, 6.5, 6.5 Hz, 1H), 3.64-3.45 (m, 4H), 3.58 (d, *J* = 10.0 Hz, 1H), 3.33 (s, 3H), 3.32 (s, 3H), 3.31 (s, 3H), 3.26 (d, *J* = 15.5 Hz, 1H), 3.11 (d, *J* = 14.5 Hz, 1H), 2.71 (d, *J* = 12.0 Hz, 1H), 2.54 (dd, *J* = 5.0, 2.5 Hz, 1H), 2.49 (dd, *J* = 6.0, 3.0 Hz, 1H), 2.46 (dd, *J* = 6.0, 2.5 Hz, 1H), 2.44 (dd, *J* = 6.5, 2.5 Hz, 1H), 2.41 (m, 1H), 2.35 (m, 1H), 2.32 (m, 1H), 2.25 (dd, *J* = 13.0, 3.0 Hz, 1H), 2.08-2.03 (m, 1H), 2.04 (s, 1H), 2.01 (t, *J* = 2.5 Hz, 1H), 1.98 (s, 3H), 1.95-1.86 (m, 5H), 1.86 (s, 3H), 1.72 (app d, *J* = 14.0 Hz, 1H), 1.60 (ddd, *J* = 14.0, 2.5, 2.5 Hz, 1H), 1.47-1.37 (m, 2H), 1.13 (q, *J* = 12.0 Hz, 1H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 6.0 Hz, 3H); ^{13}C NMR (125 MHz) δ 165.6, 161.3, 159.0, 144.4, 142.1, 141.7, 137.9, 137.3, 137.2, 136.3, 134.2, 133.7, 130.0, 128.3, 121.0, 119.3, 110.1, 100.0, 89.2, 80.5, 80.2, 79.4, 78.0, 76.8, 73.5, 73.1, 72.9, 71.1, 70.0, 69.2, 68.6, 66.9, 64.4, 56.6, 55.7, 48.2, 41.3, 39.1, 39.0, 39.0, 37.0, 35.6, 35.0, 34.4, 32.9, 32.6, 31.8, 30.5, 29.7, 25.8, 14.3, 13.5, 13.3, 6.0; HRMS calc. for $C_{54}H_{72}N_2O_{13}$ $[M+Na]^+$ 979.4932, found 979.4939. Copies of ^1H NMR and ^{13}C NMR spectra of compound **34** are included below.



45,46-Dehydrobromo-phorboxazole A (35).

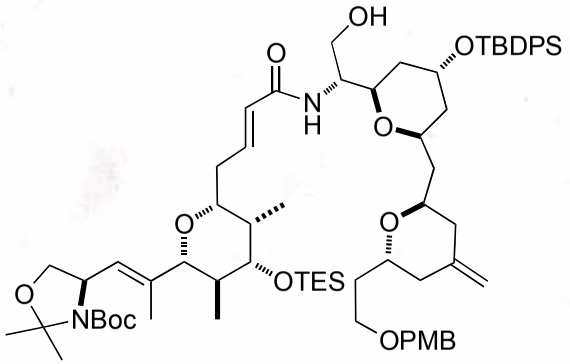
To a solution of **34** (3.5 mg, 3.6 μmol) in THF (4.4 mL) was added 6% aqueous HCl (0.9 mL). The mixture was stirred for 30 h, then washed with saturated aqueous $NaHCO_3$ (5 mL). The aqueous phase was extracted with ethyl acetate (5 × 5 mL), and the combined organic phase was dried over Na_2SO_4, filtered, concentrated and purified by flash chromatography (ethyl acetate) to give **35** (2.3 mg, 2.4 μmol, 68%) as a white film: R_f 0.45 (ethyl acetate); $[\alpha]_D^{23}$ +32.9 (c 0.85, $CHCl_3$); IR 3567, 3331, 2924, 1773, 1718, 1684, 1654, 1647, 1636, 1577, 1570, 1559, 1542, 1534, 1508, 1498, 1490, 1458, 1434, 1376, 1260, 1188, 1090, 885, 812 cm^{-1}; ^1H NMR (800 MHz, $CHCl_3$) δ 7.58 (s, 1H,), 7.43 (s, 1H), 6.69 (ddd, *J* = 16.0, 10.0, 7.0 Hz, 1H), 6.29 (m, 1H), 6.25 (s, 1H), 5.93 (m, 2H), 5.62 (dd, *J* = 16.0, 7.5 Hz, 1H), 5.37 (d, *J* = 9.6 Hz, 1H), 5.32 (s, 1H), 4.99 (s, 1H), 4.74 (d, *J* = 10.4 Hz, 1H), 4.63 (s, 1H), 4.52 (dd, *J* = 12.8, 4.8 Hz, 1H), 4.41 (app s, 1H), 4.32 (app t, *J* = 9.6 Hz, 1H), 4.17 (m, 1H), 4.07 (app t, *J* = 12.0 Hz, 1H), 4.00 (m, 1H), 3.79 (ddd, *J* = 12.3, 7.9, 2.0 Hz, 1H), 3.74 (dddd, *J* = 11.8, 11.8, 4.6, 4.6 Hz, 4H), 3.58 (d, *J* = 10.0 Hz, 1H), 3.56 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.48 (s, 1H), 3.37 (s, 3H), 3.32 (s, 3H), 3.15 (d, *J* = 15.2 Hz, 1H), 3.07 (d, *J* = 15.2 Hz, 1H), 2.71 (bd, *J* = 12.5 Hz, 1H), 2.51 (m, 2H), 2.45 (m, 2H), 2.34 (m, 4H), 2.04 (bd, *J* = 13.0 Hz 1H), 2.01 (m, 1H), 1.98 (s, 3H), 1.97 (m, 1H), 1.90 (m, 1H), 1.83 (s, 3H), 1.73 (d, *J* = 12.0 Hz, 1H), 1.6-1.5 (m, 1H), 1.45 (ddd, *J* = 13.2, 10.2, 3.1 Hz, 1H), 1.37 (ddd, *J* = 11.8, 11.8, 1.6 Hz, 1H), 1.11 (q, *J* = 12.0 Hz, 1H), 0.97 (d, *J* = 7.0 Hz, 3H), 0.77 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (75 MHz) δ 165.6, 161.2, 159.9, 144.3, 141.9, 141.6, 137.8, 137.5, 137.4, 137.2, 135.8, 134.0, 133.6, 129.6, 128.6, 128.1, 120.9, 119.2, 118.4, 110.0, 96.5, 89.1, 80.4, 80.1, 79.2, 77.9, 77.1, 73.4, 72.9, 72.4, 70.8, 69.9, 69.0, 68.5, 66.8, 64.3, 56.5, 55.7, 41.1, 40.4, 39.6, 38.9, 36.8, 34.9, 34.3, 32.9, 32.4, 31.6, 30.4, 25.7, 14.1, 13.4, 13.2, 5.9; HRMS calc. for $C_{54}H_{72}N_2O_{13}$ $[M+Na]^+$ 965.4771, found 965.4763; Copies of ^1H NMR and ^{13}C NMR spectra of **35** are included below.

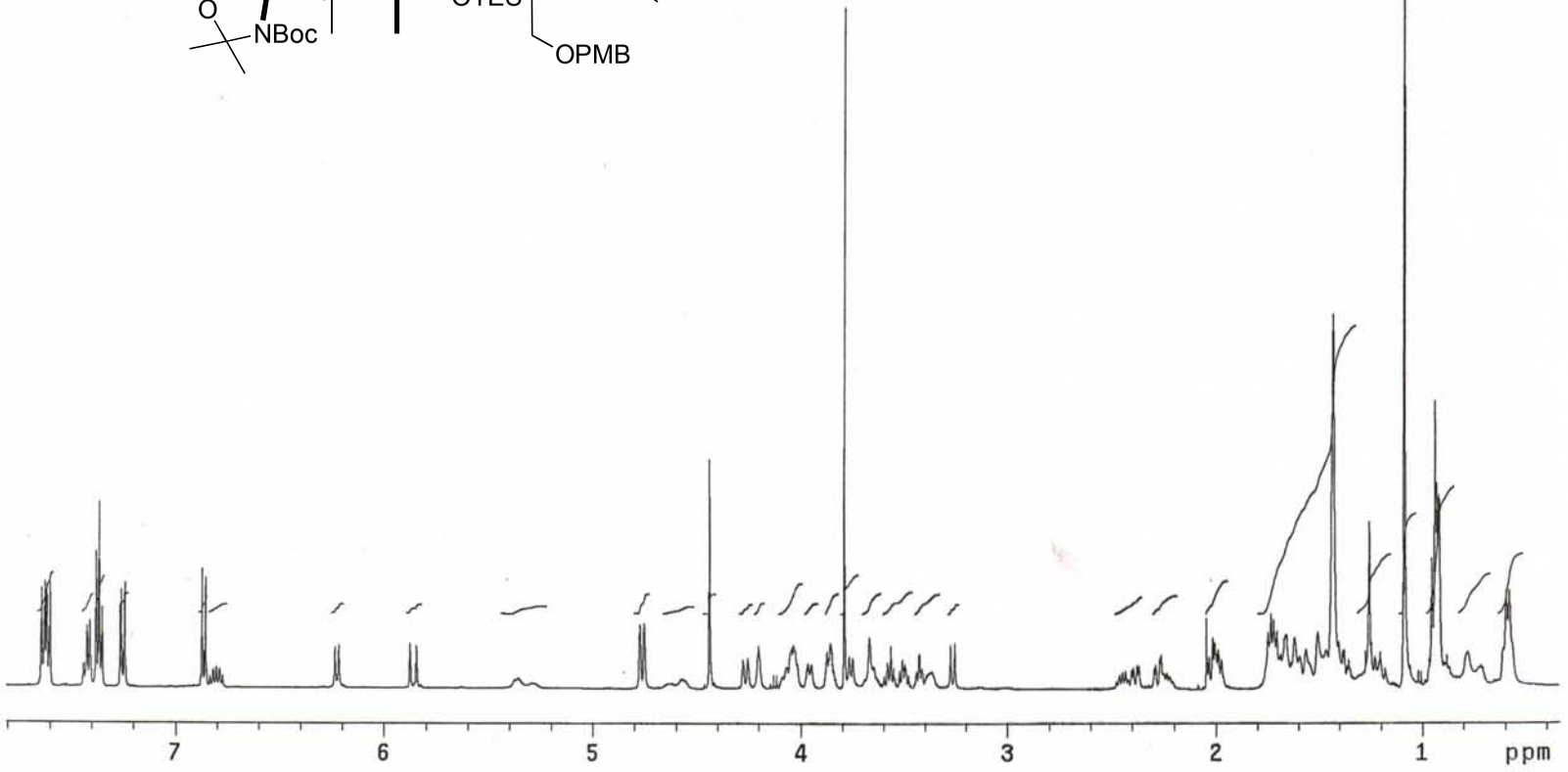
Mac Amide

STANDARD PROTON PARAMETERS

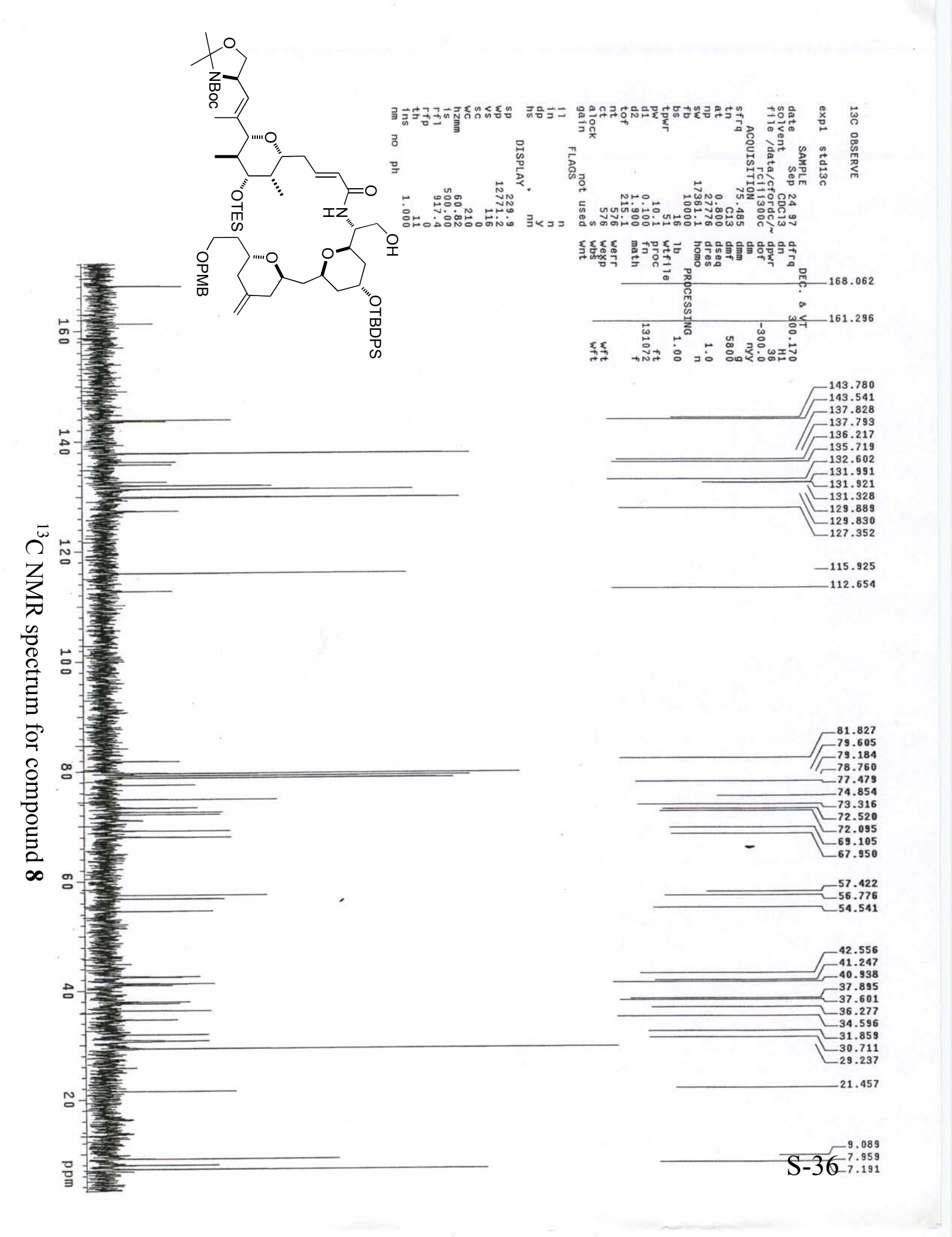
exp3 s2pul

SAMPLE		DEC. & VT	
date	Sep 24 97	dfrq	499.870
solvent	CDCl3	dn	H1
file	/data/cfordc/~	dpwr	15
	rciii300h	dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.5	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	168.1		
wp	3734.6		
vs	67		
sc	0		
wc	210		
hzmm	17.78		
is	315.26		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	1.200		
ai cdc ph			





^{1}H NMR spectrum for compound **8**



^{13}C NMR spectrum for compound **8**

oxazole

STANDARD PROTON PARAMETERS

exp1 s2pul

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date	Nov 19 97	dfrq	499.870
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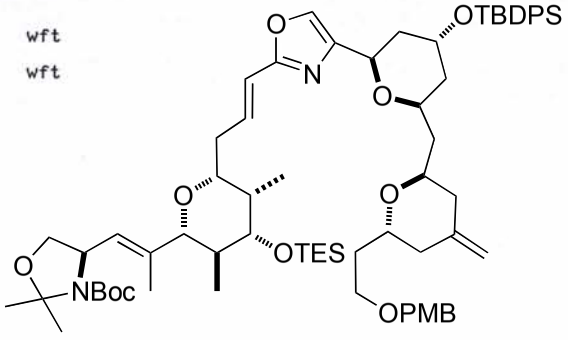
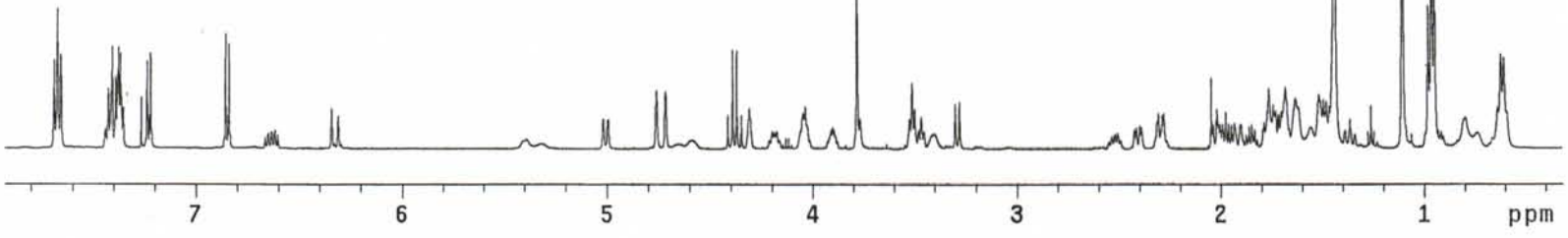
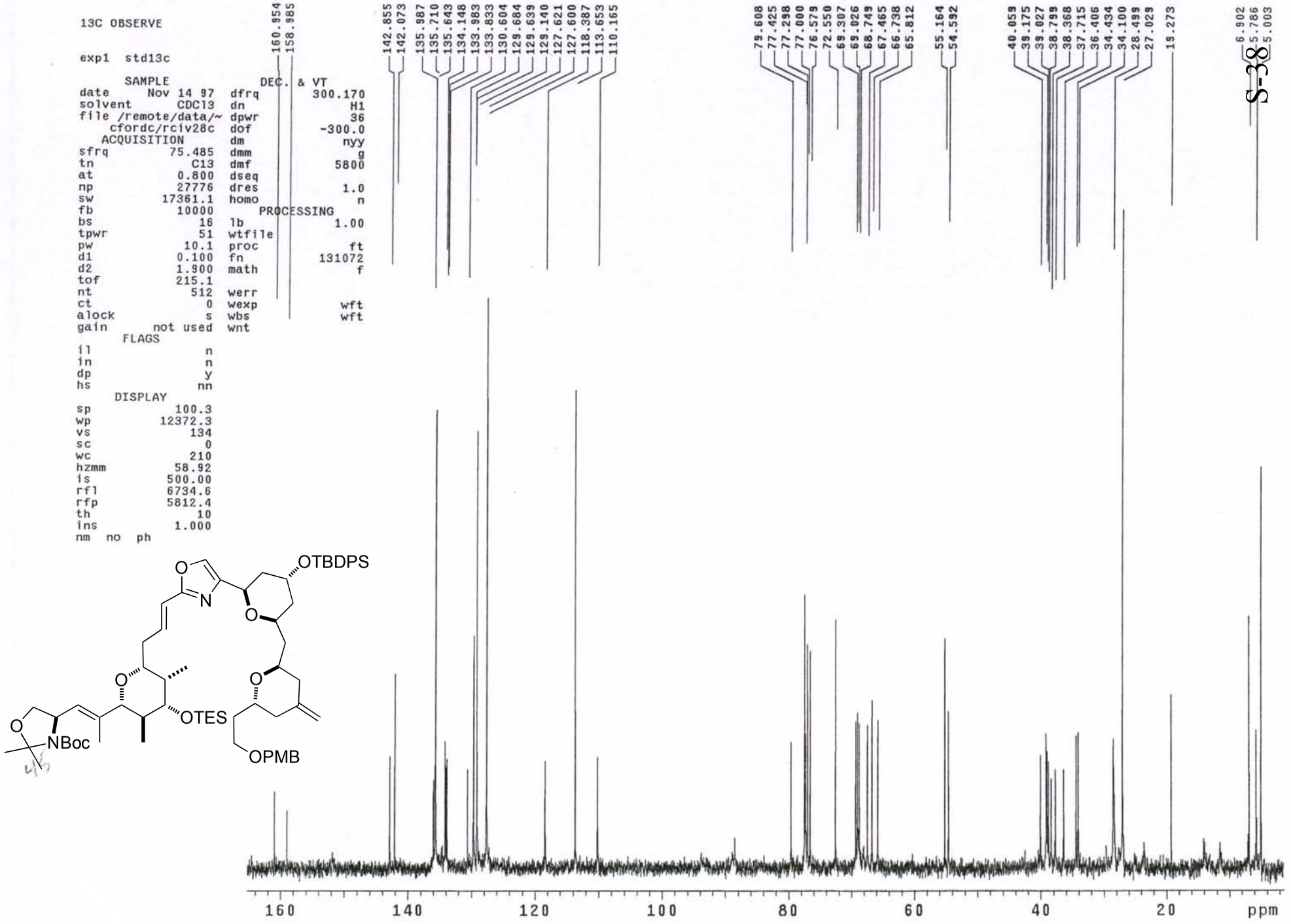
file	/export/home/~	dpwr	15
data	/cfordc/rciv30	dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.1	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	159.2		
wp	3803.3		
vs	58		
sc	0		
wc	210		
hzmm	18.11		
is	33.57		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	100.000		

ai cdc ph





^{1}H NMR spectrum for compound **10**



^{13}C NMR spectrum for compound **10**

```
STANDARD PROTON PARAMETERS

exp3  s2pul

      SAMPLE
date      Nov 21 97
solvent       CDCl3
file /remote/data/~
    cfordc/rciv32h
   ACQUISITION
sfrq        499.871
tn               H1
at           2.001
np           40000
sw          9997.5
fb            6000
bs              16
tpwr            58
pw             7.1
d1           1.500
tof         1504.1
nt              32
ct               0
alock            n
gain      not used
      FLAGS
il               n
in               n
dp               y
hs              yn
     DISPLAY
sp           273.8
wp          3703.7
vs              66
sc               0
wc             210
hzmm         17.64
is           33.57
rfl         4614.4
rfp         3619.1
th               7
ins        100.000
ai  cdc  ph

      DEC. & VT
dfrq        499.870
dn               H1
dpwr             15
dof               0
dm              nnn
dmm               c
dmf             200
dseq
dres            1.0
homo              n
     PROCESSING
lb              0.10
wtfile
proc             ft
fn           131072
math              f

werr
wexp            wft
wbs
wnt             wft
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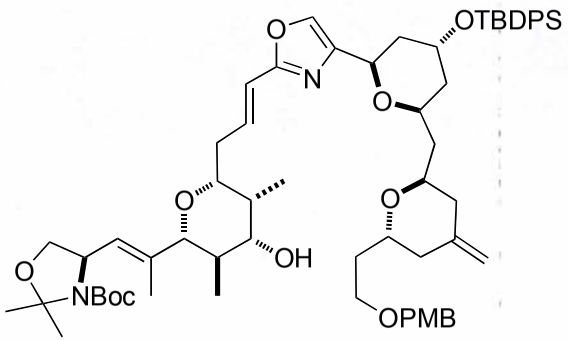
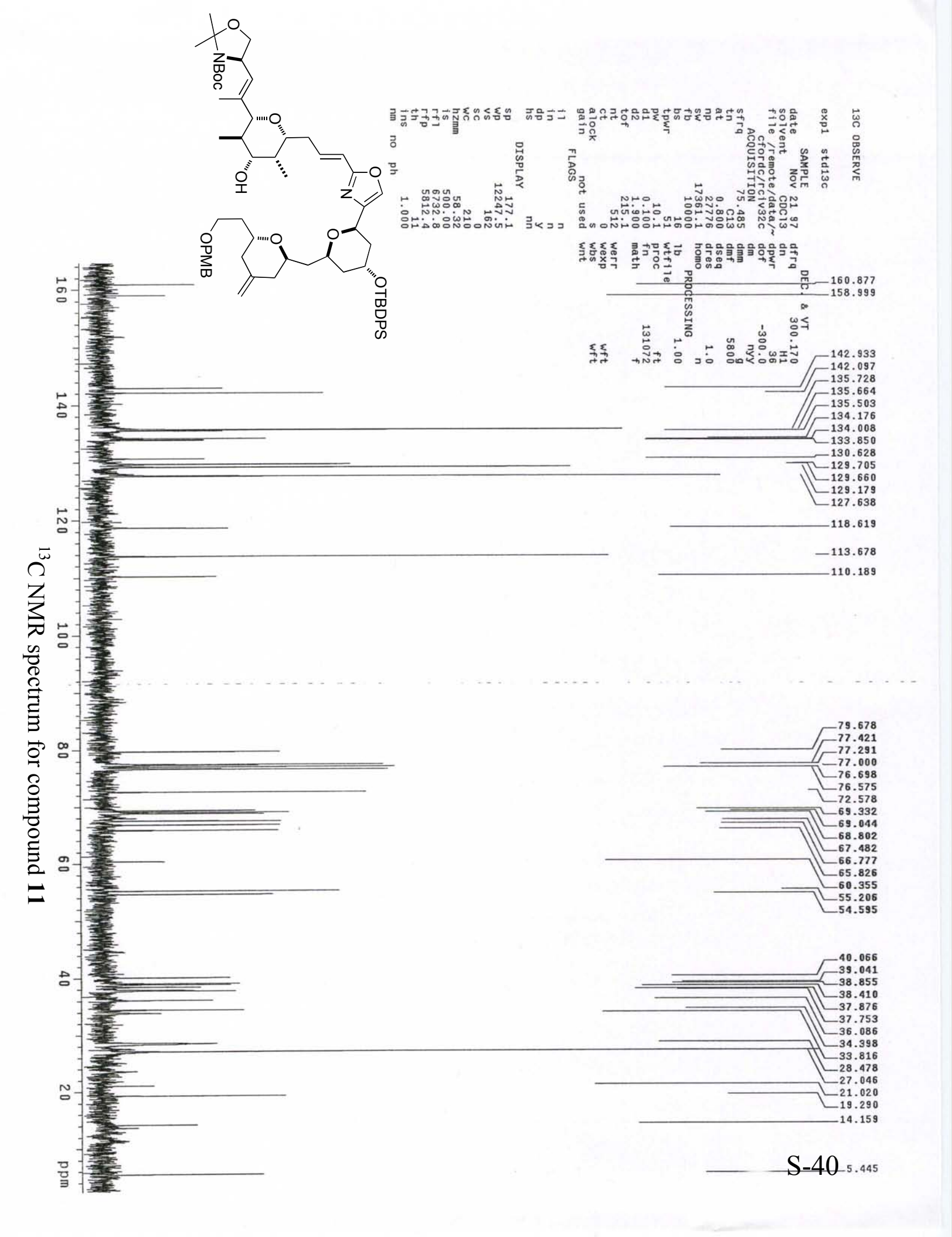


^{1}H NMR spectrum for compound **11**



^{13}C NMR spectrum for compound **11**

STANDARD PROTON PARAMETERS

exp3 s2pul

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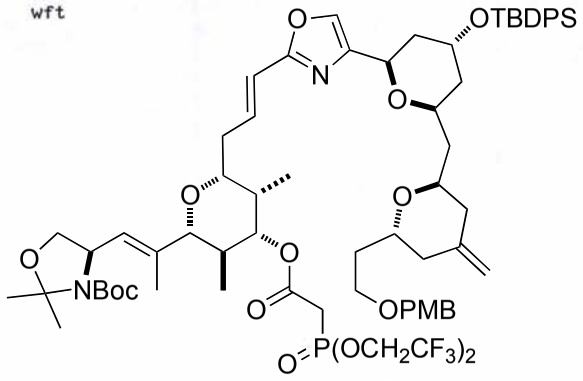
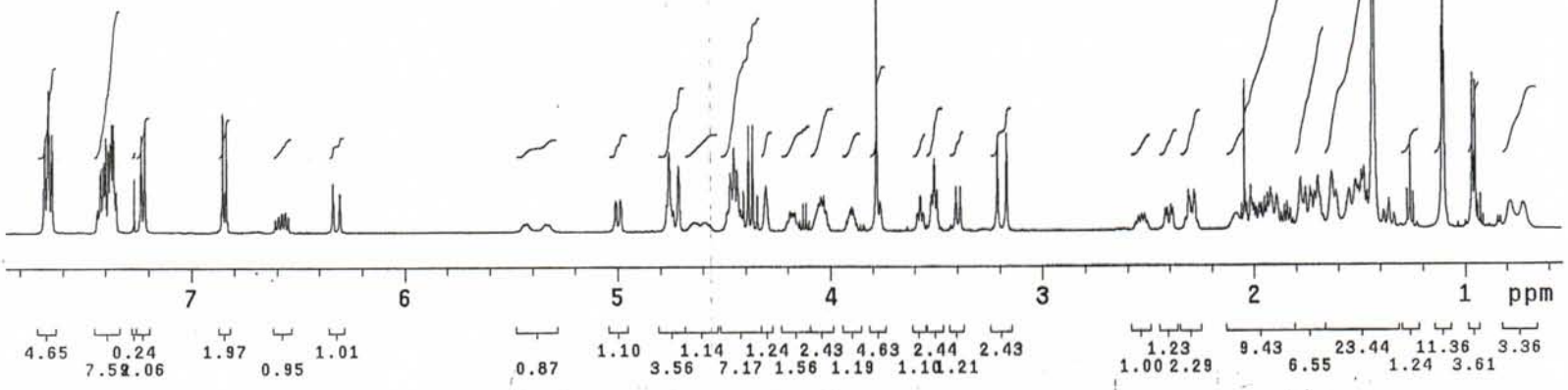
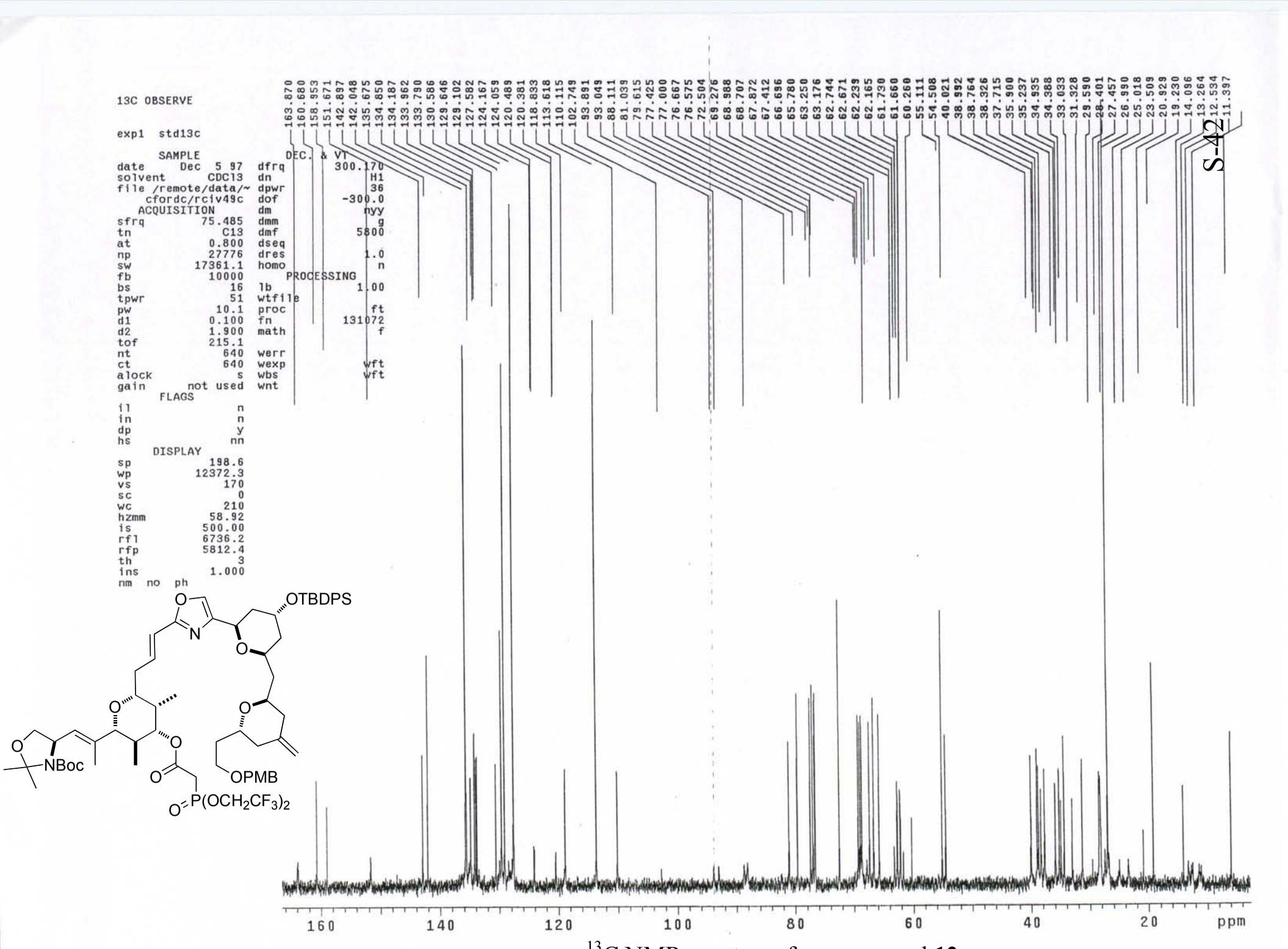
file	/remote/data/~	dpwr	15
	cfordc/rciv47h	dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.1	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	0	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	268.7		
wp	3662.8		
vs	89		
sc	0		
wc	210		
hzmm	17.44		
is	896.30		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	2.600		
ai cdc ph			





^{1}H NMR spectrum for compound **12**



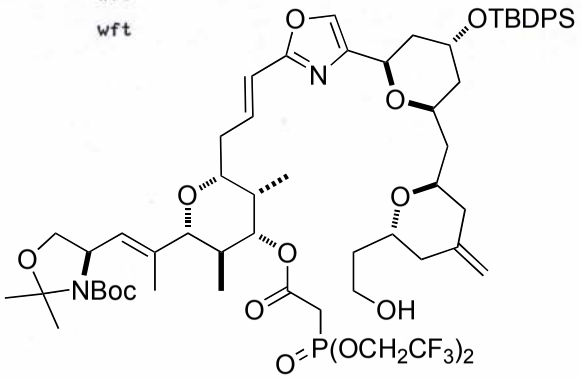
^{13}C NMR spectrum for compound **12**

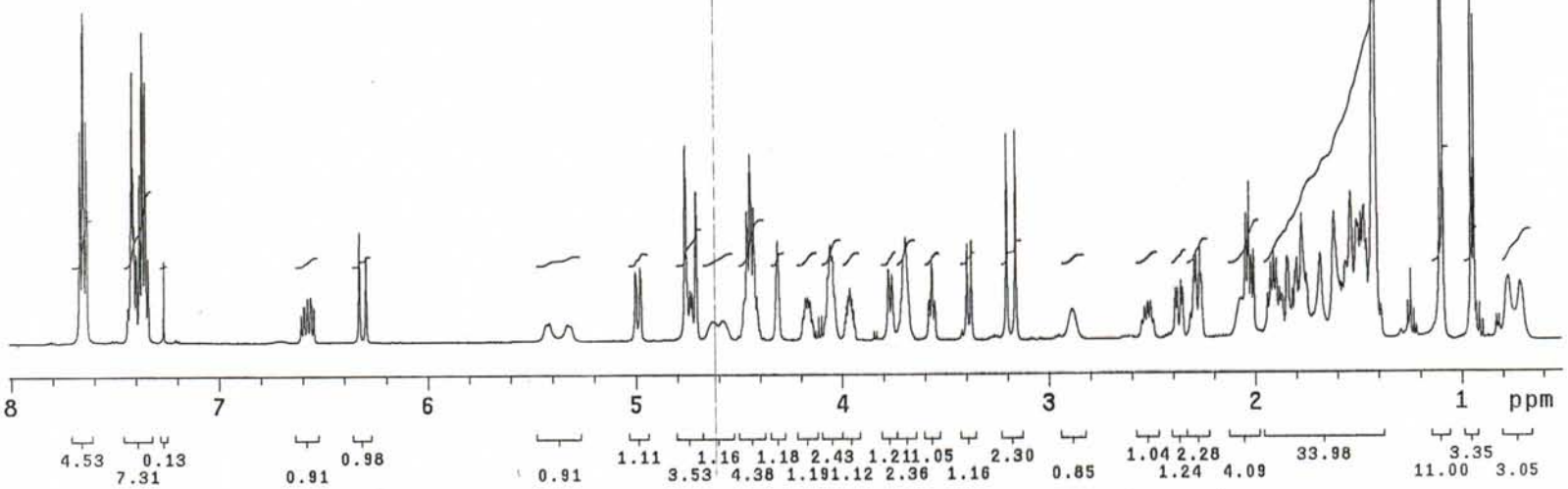
Alcohol (2)

STANDARD PROTON PARAMETERS

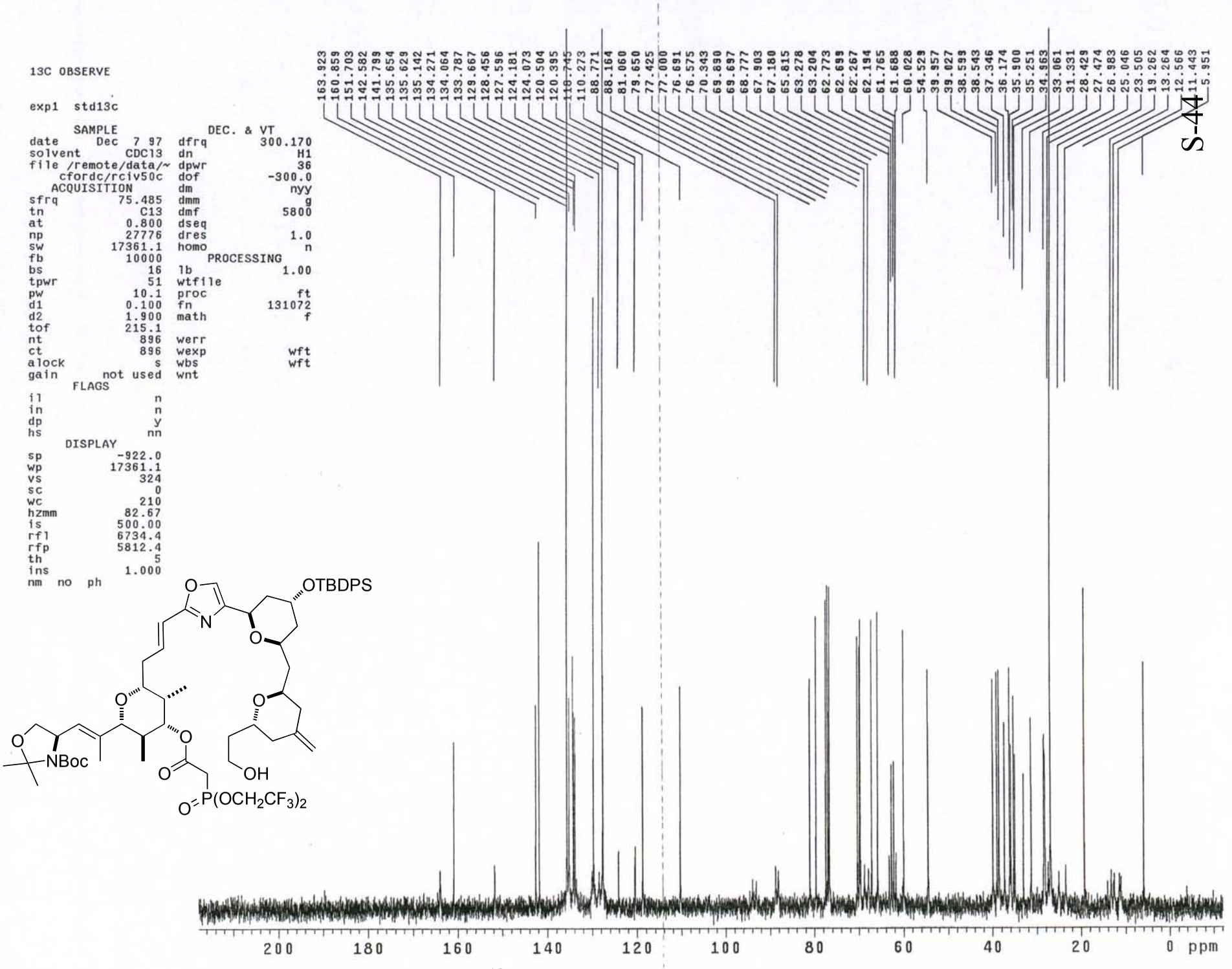
exp3 s2pul

SAMPLE		DEC. & VT	
date	Dec 7 97	dfrq	499.870
solvent	CDCl3	dn	H1
file	/remote/data/~	dpwr	15
	cfordc/rciv50h	dof	0
ACQUISITION		dm	nnn
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.1	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	254.3		
wp	3749.0		
vs	170		
sc	0		
wc	210		
hzmm	17.85		
is	397.17		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	1.400		
ai cdc ph			





^{1}H NMR spectrum for compound **12a**



^{13}C NMR spectrum for compound **12a**

Add. no carbon!

STANDARD PROTON PARAMETERS

exp1 s2pul

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date	Dec 8 97	dfrq	499.870
solvent	CDCl3	dn	H1
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data	cfordc/rciv51	dof	0
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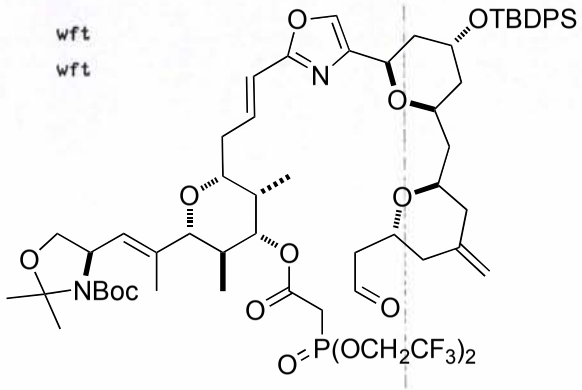
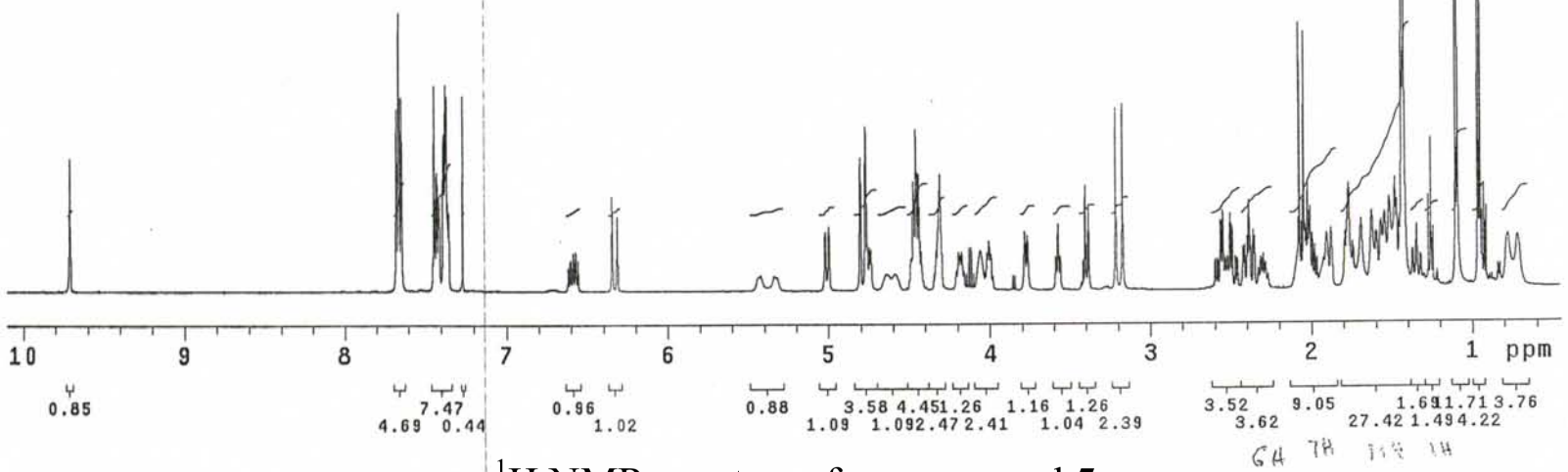
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	PROCESSING	
bs	16	lb	0.10
tpwr	58	wtfile	
pw	7.1	proc	ft
d1	1.500	fn	131072
tof	1504.1	math	f
nt	32		
ct	32	werr	
alock	n	wexp	wft
gain	not used	wbs	
FLAGS		wnt	wft
il	n		
in	n		
dp	y		
hs	yn		
DISPLAY			
sp	227.1		
wp	4822.0		
vs	138		
sc	0		
wc	210		
hzmm	22.96		
is	267.78		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	105.000		
ai cdc ph			





^{1}H NMR spectrum for compound **5**

Mac. protected. Mixture?


```
STANDARD PROTON PARAMETERS

exp1  s2pul

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data/cfordc/rciv52~   dof              0
                _1h   dm              nnn
   ACQUISITION        dmm              c
sfrq        499.871   dmf            200
tn               H1   dseq
at            2.001   dres           1.0
np            40000   homo             n
sw           9997.5        PROCESSING
fb            6000    lb            0.10
bs              16    wtfile
tpwr            58    proc             ft
pw             7.1    fn           131072
d1           1.500    math             f
tof         1504.1
nt              32    werr
ct              32    wexp           wft
alock            n    wbs
gain      not used    wnt            wft
      FLAGS
il               n
in               n
dp               y
hs              yn
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sp           267.8
wp          3613.2
vs             208
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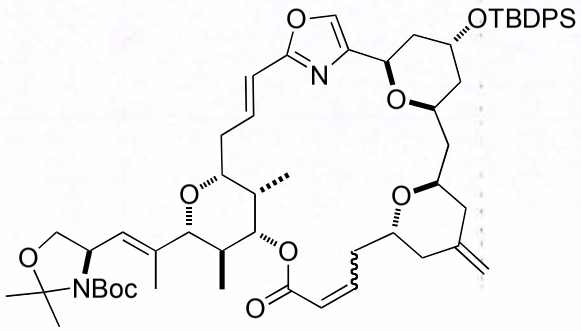
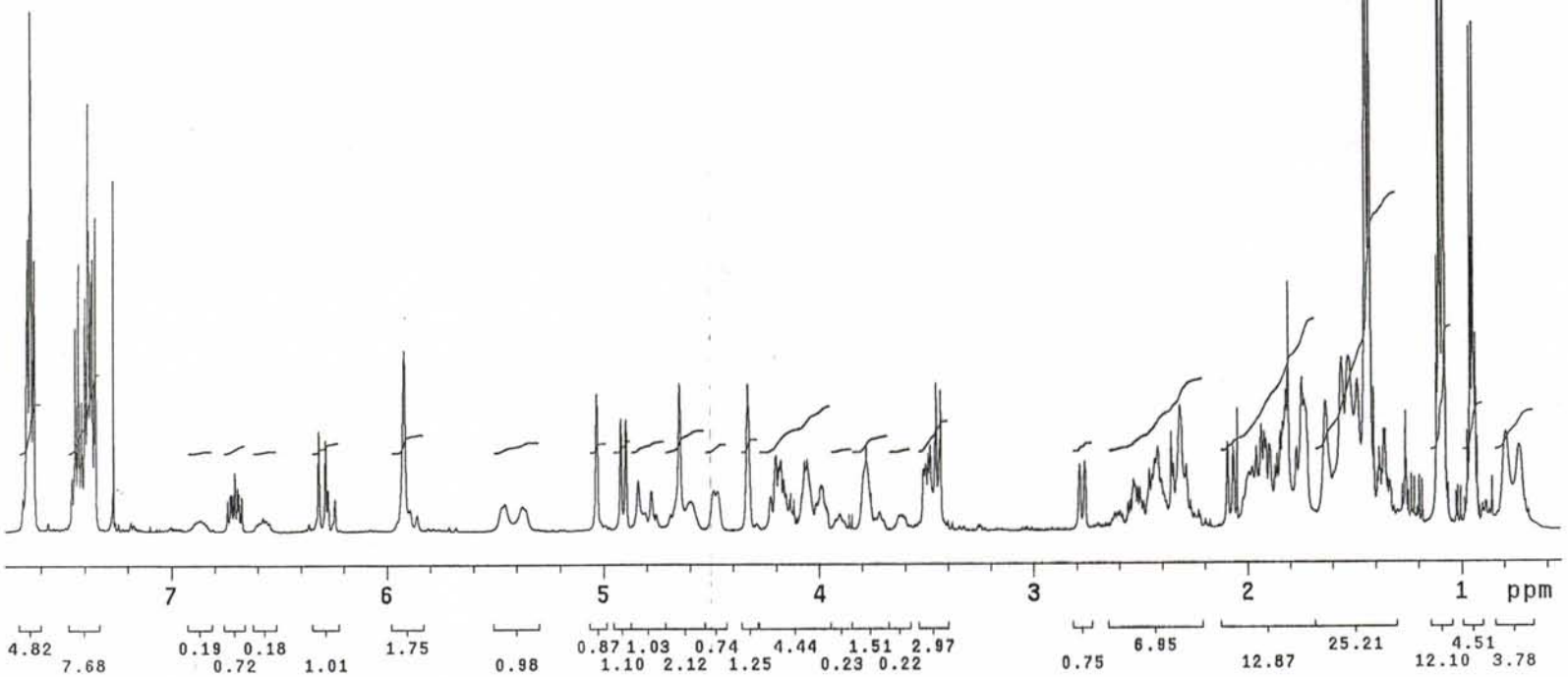
rfp         3619.1
th               7
ins        100.000
ai  cdc  ph
```





^{1}H NMR spectrum for the mixture of compound **14** and **15** (**14** : **15** = 4 : 1)

STANDARD PROTON PARAMETERS

exp1 s2pul

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		dof	0
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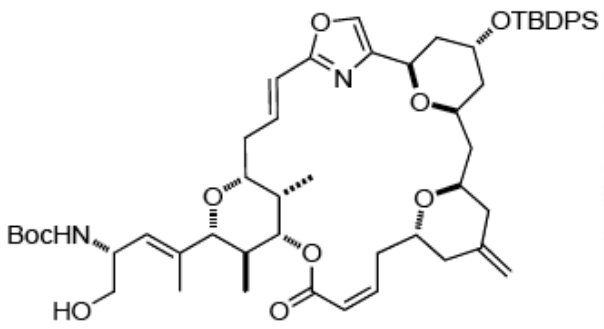
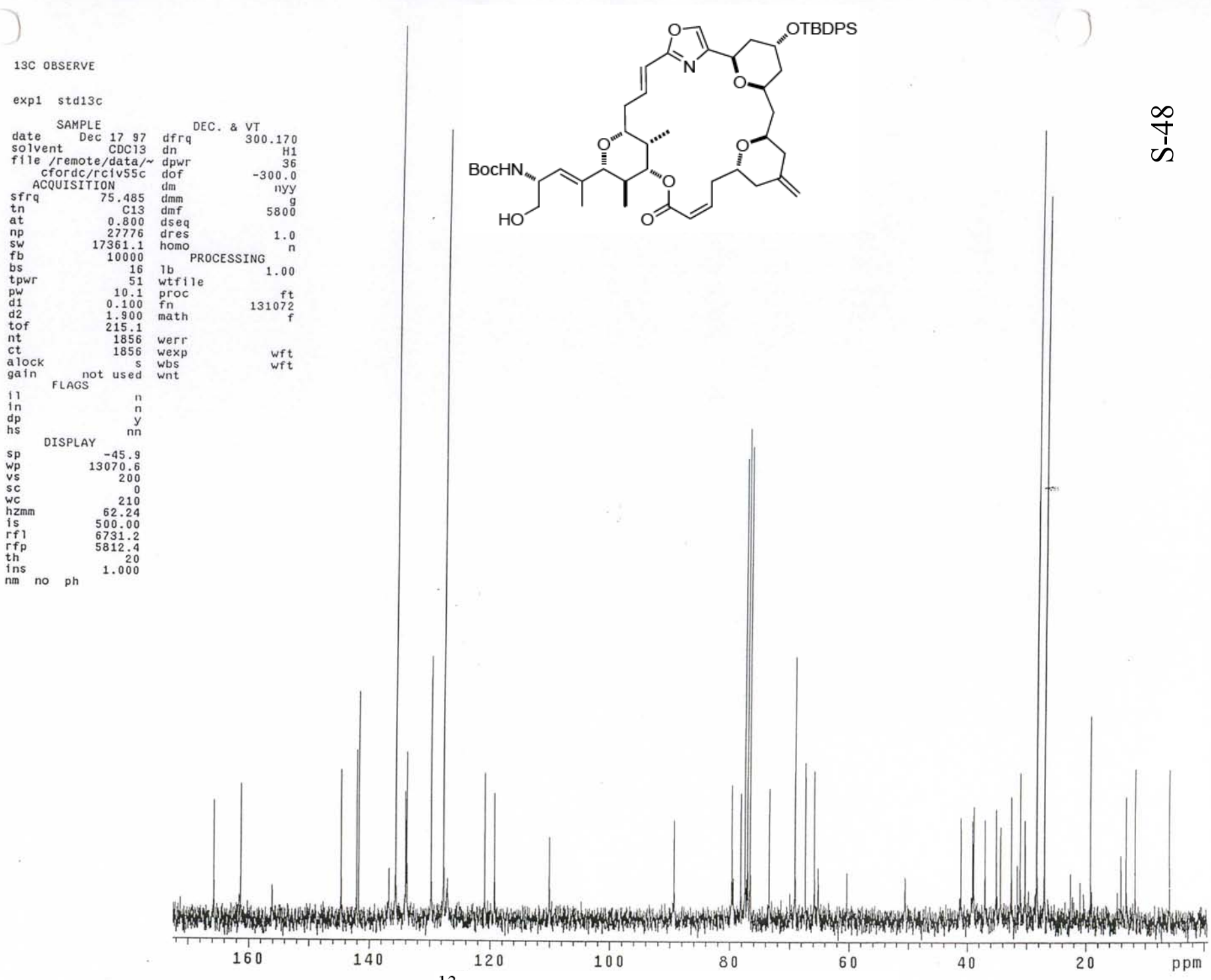
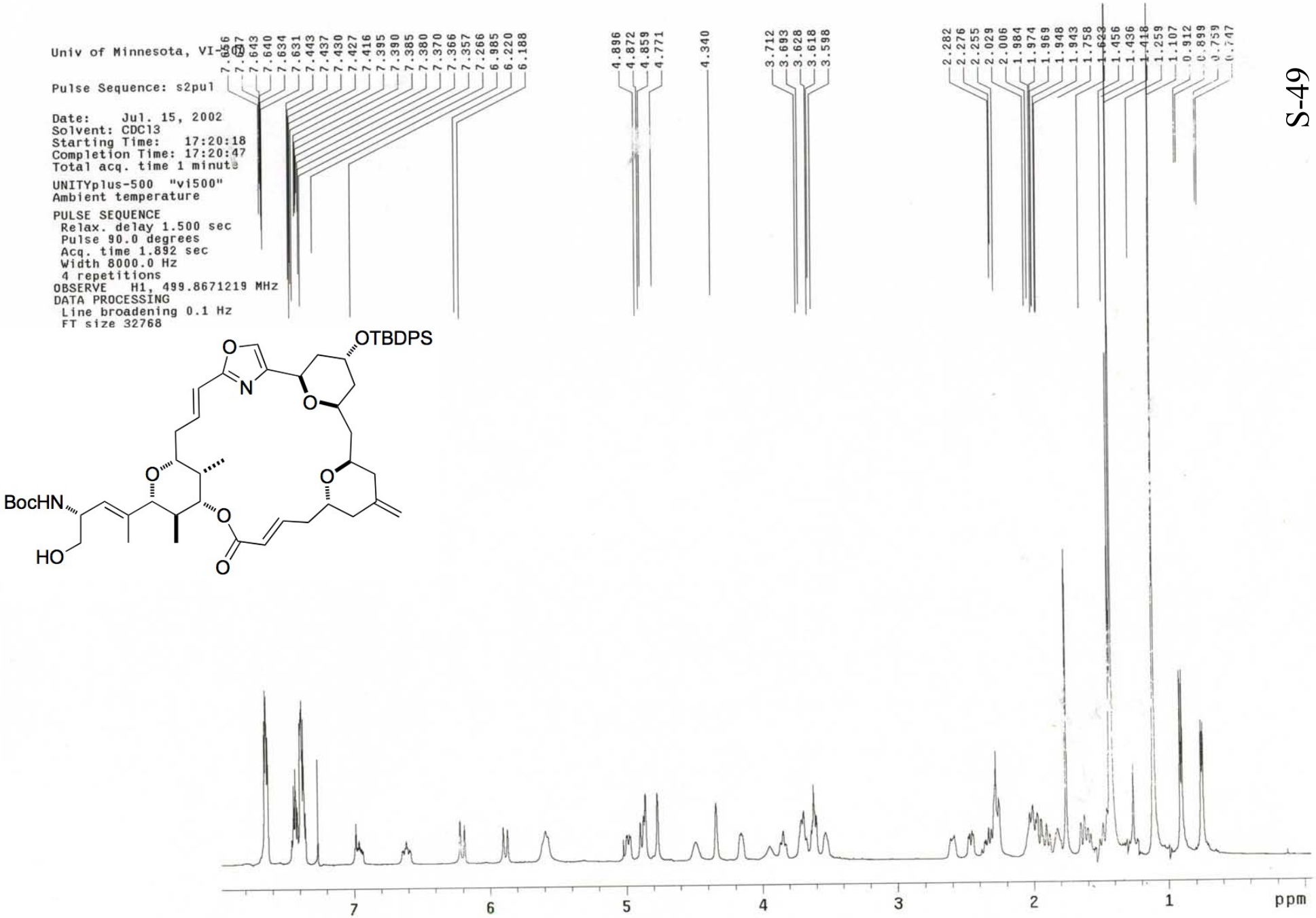
sfrq	499.871	dmm	c
tn	H1	dmf	200
at	2.001	dseq	
np	40000	dres	1.0
sw	9997.5	homo	n
fb	6000	DEC2	
bs	16	dfrq2	0
tpwr	58	dn2	
pw	7.1	dpwr2	1
d1	1.500	dof2	0
tof	1504.1	dm2	n
nt	16	dmm2	c
ct	16	dmf2	200
alock	n	dseq2	
gain	not used	dres2	1.0
FLAGS		homo2	n
il	n	PROCESSING	
in	n	lb	0.10
dp	y	wtfile	
hs	yn	proc	ft
DISPLAY		fn	131072
sp	284.9	math	f
wp	3697.4		
vs	163	werr	
sc	0	wexp	wft
wc	210	wbs	
hzmm	17.61	wnt	wft
is	33.57		
rfl	4614.4		
rfp	3619.1		
th	7		
ins	100.000		
ai cdc ph			



^{1}H NMR spectrum for compound **16**



^{13}C NMR spectrum for compound **16**



^{1}H NMR spectrum for compound **17**

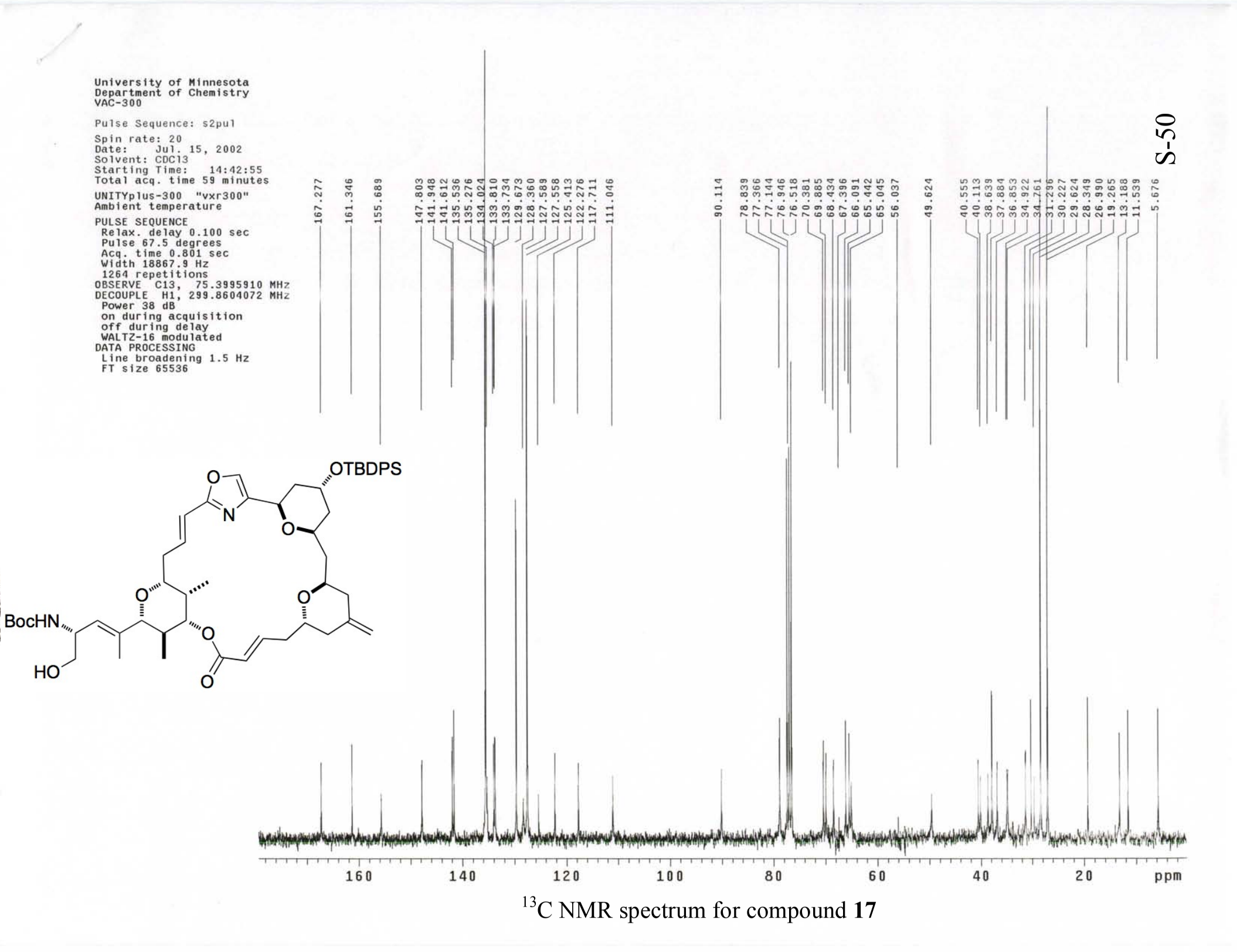
University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pul

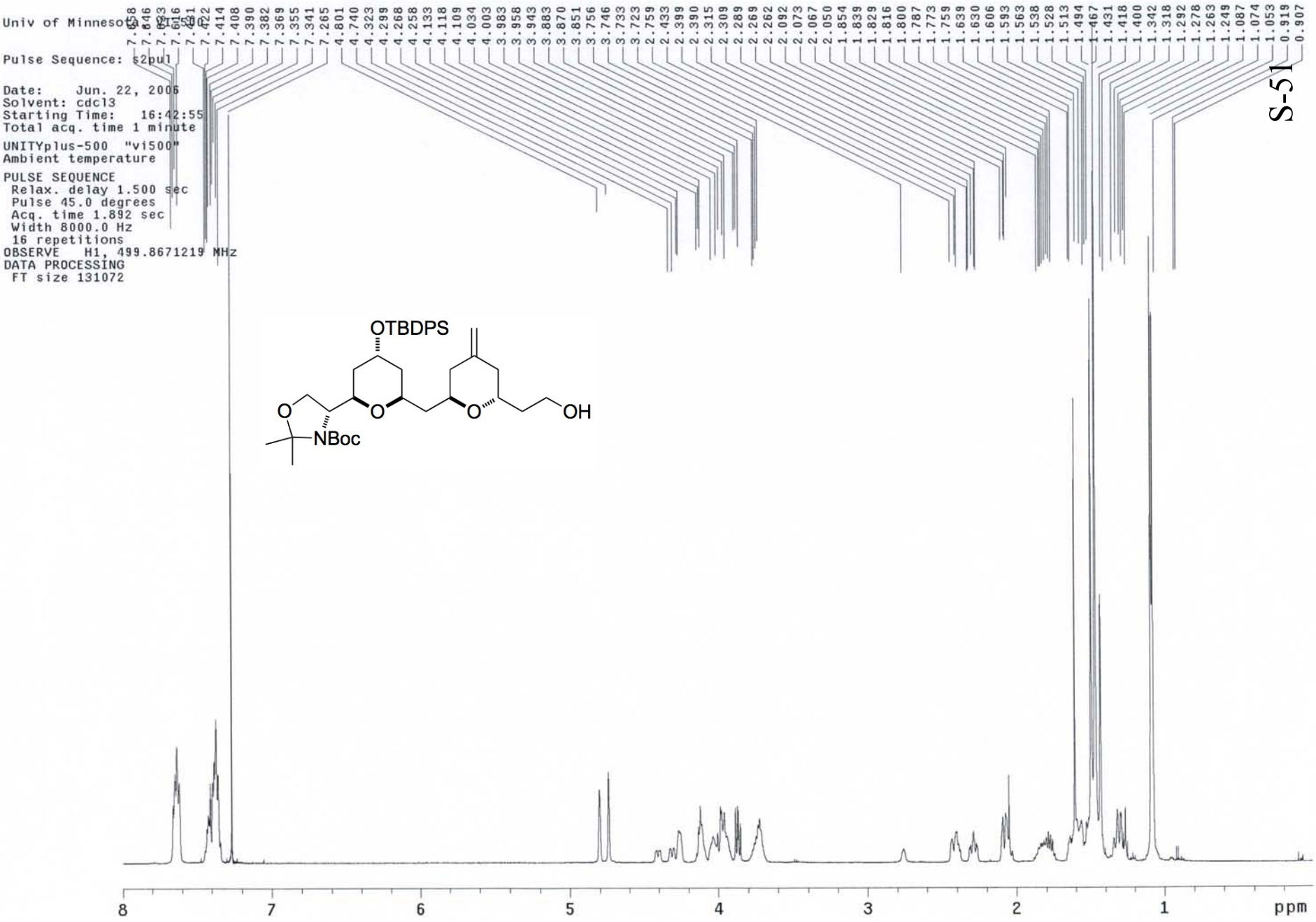
Spin rate: 20
Date: Jul. 15, 2002
Solvent: CDCl3
Starting Time: 14:42:55
Total acq. time 59 minutes

UNITYplus-300 "vxr300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18867.9 Hz
1264 repetitions
OBSERVE C13, 75.3995910 MHz
DECOUPLE H1, 299.8604072 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536



^{13}C NMR spectrum for compound **17**



^{1}H NMR spectrum for compound **51**

Univ of Minnesota, [illegible]

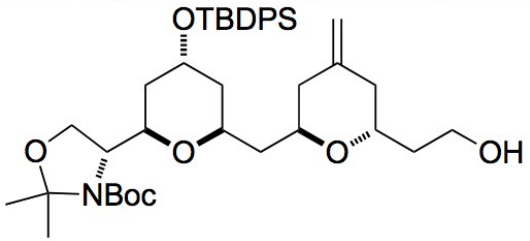
Pulse Sequence: s2pul

Date: Jul. 31, 2005
Solvent: cdcl3
File: BW-Phorb-RCM-C3alcohol-C
Starting Time: 16:14:27
Completion Time: 17:20:07
Total acq. time 65 minutes

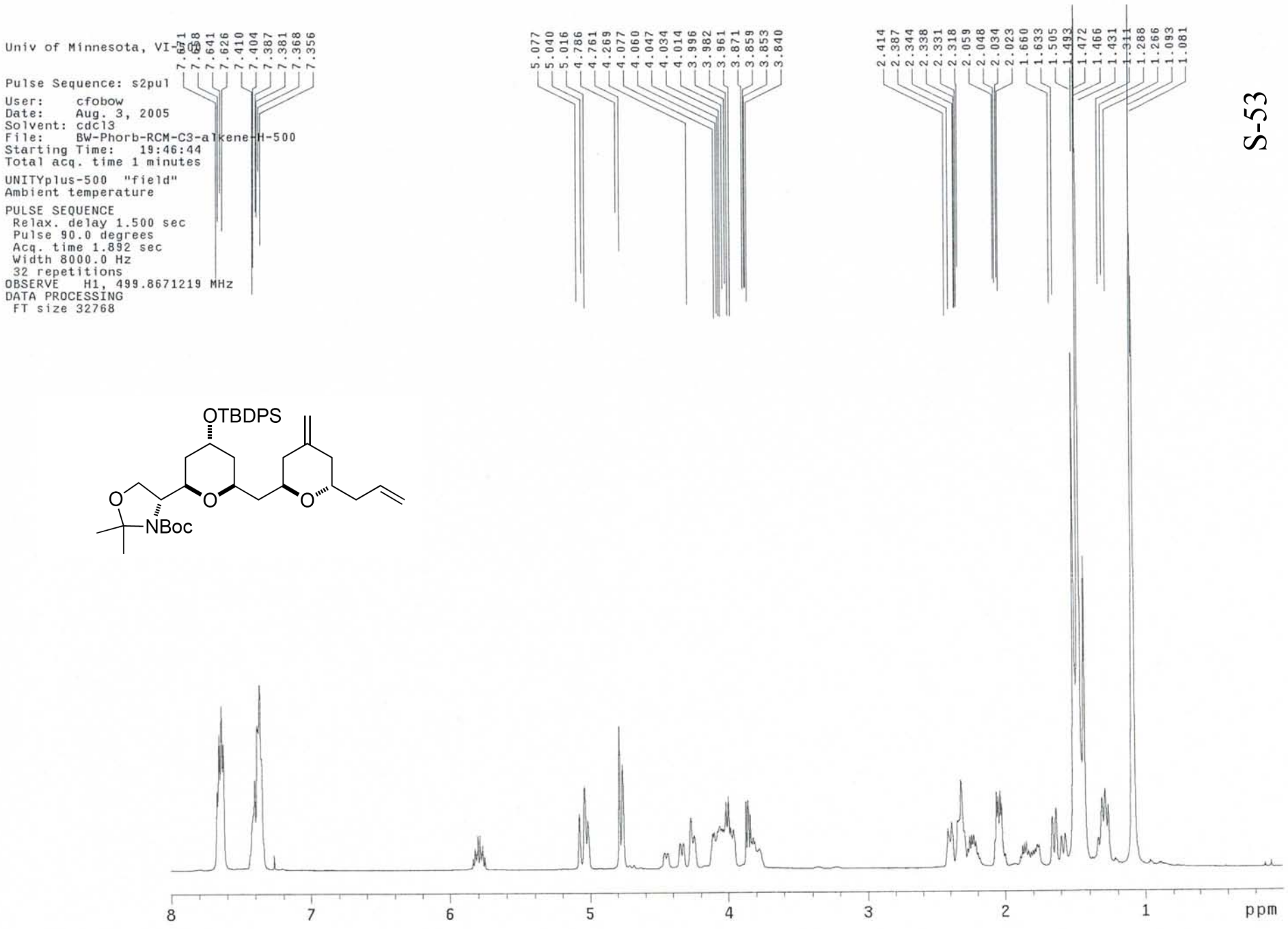
UNITYplus-500 "vi500"
Ambient temperature

PULSE SEQUENCE
Relax. delay 5.000 sec
Pulse 67.5 degrees
Acq. time 0.960 sec
Width 32989.7 Hz
500 repetitions
OBSERVE C13, 125.6916844 MHz
DECOUPLE H1, 499.8696213 MHz
Power 36 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536

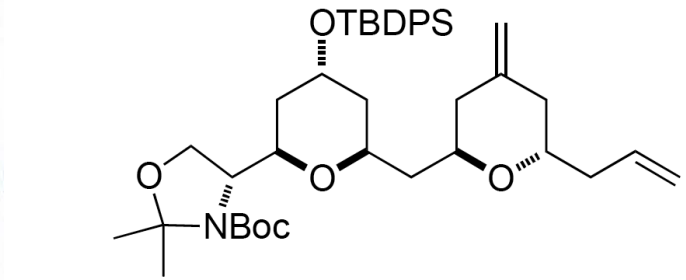
152.459
152.407
141.891
141.715
135.812
135.732
135.652
135.628
134.419
133.970
133.802
129.789
129.749
129.685
129.597
127.779
127.715
127.683
127.579
110.447
110.391
93.932
93.428
80.285
79.852
77.377
77.121
76.865
71.082
71.050
70.401
70.273
69.897
69.768
69.696
65.948
65.908
63.617
63.369
60.750
60.310
59.413
59.340
56.641
40.319
40.231
39.454
38.701
38.525
36.458
36.330
32.702
32.382
28.433
27.063
27.015
26.743
25.918
23.908
22.466
21.858
19.383
19.263
14.225
1.058



^{13}C NMR spectrum for compound **51**



^{1}H NMR spectrum for compound **21**




```
Univ of Minnesota, VI-500

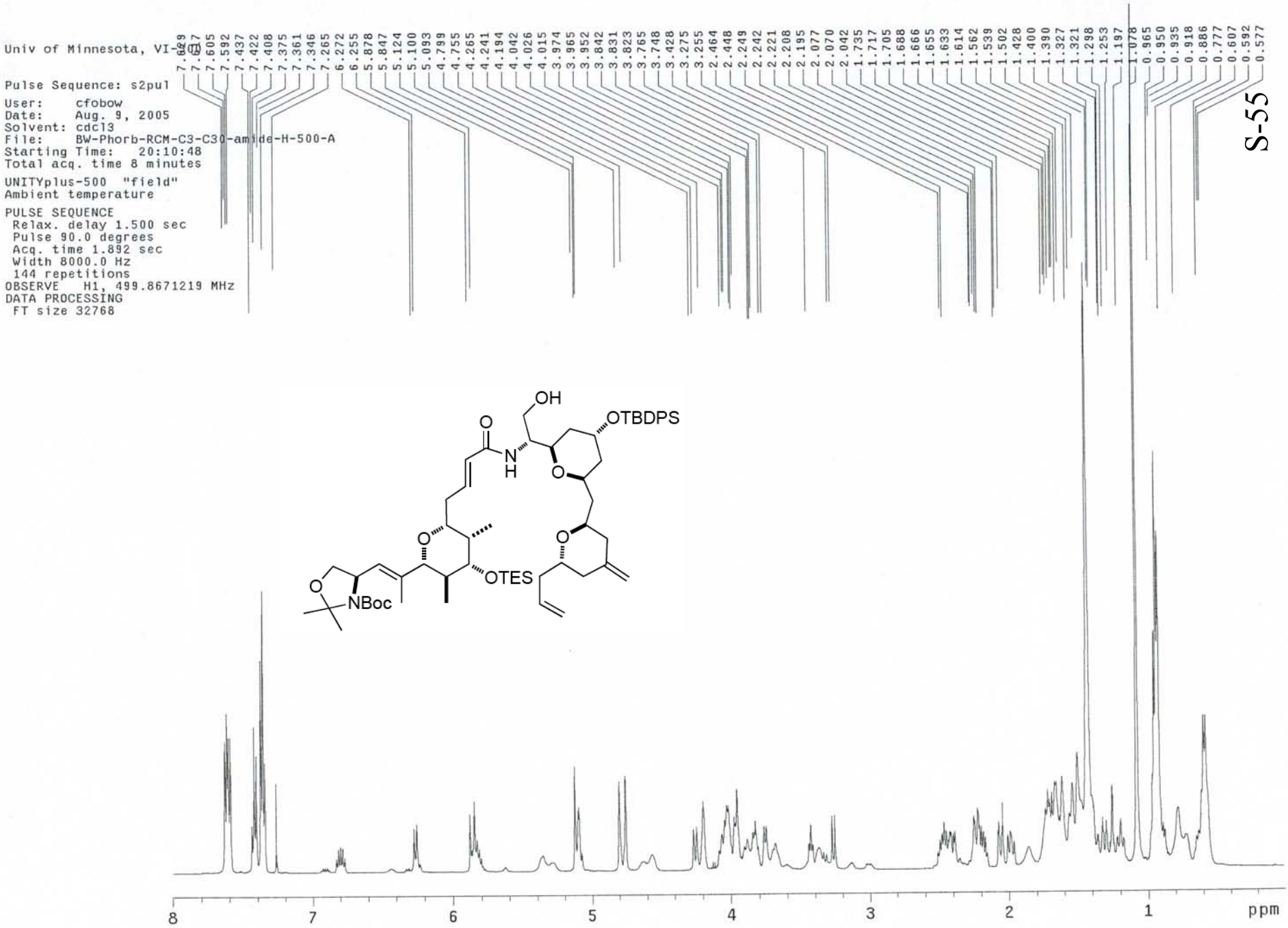
Pulse Sequence: s2pul

Date:    Aug. 3, 2005
Solvent: cdcl3
Starting Time:   19:50:03
Total acq. time 31 minutes

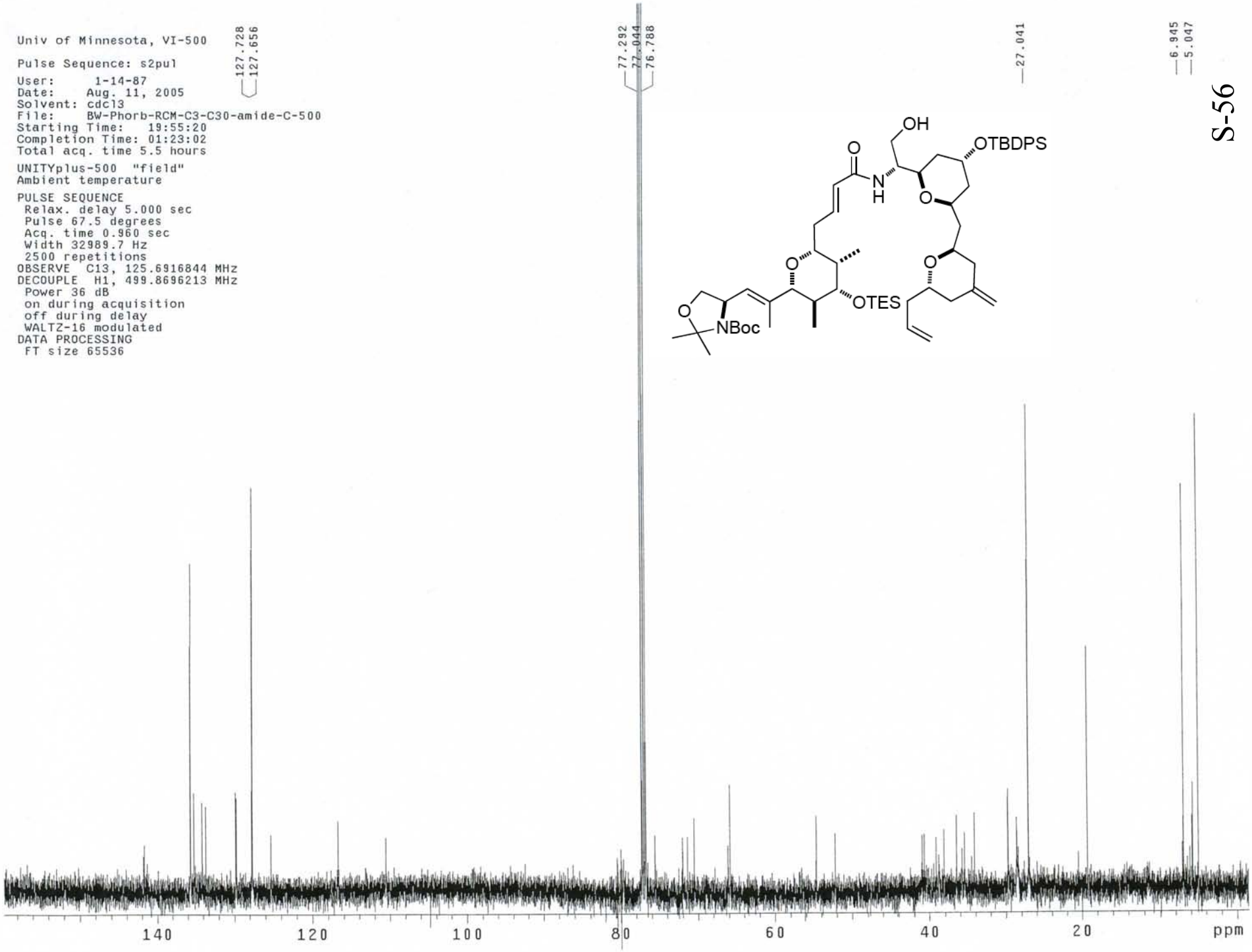
UNITYplus-500  "vi500"
Ambient temperature

PULSE SEQUENCE
 Relax. delay 5.000 sec
 Pulse 67.5 degrees
 Acq. time 0.960 sec
 Width 32989.7 Hz
 240 repetitions
OBSERVE  C13, 125.6916844 MHz
DECOUPLE  H1, 499.8696213 MHz
 Power 36 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 1.0 Hz
 FT size 65536
```

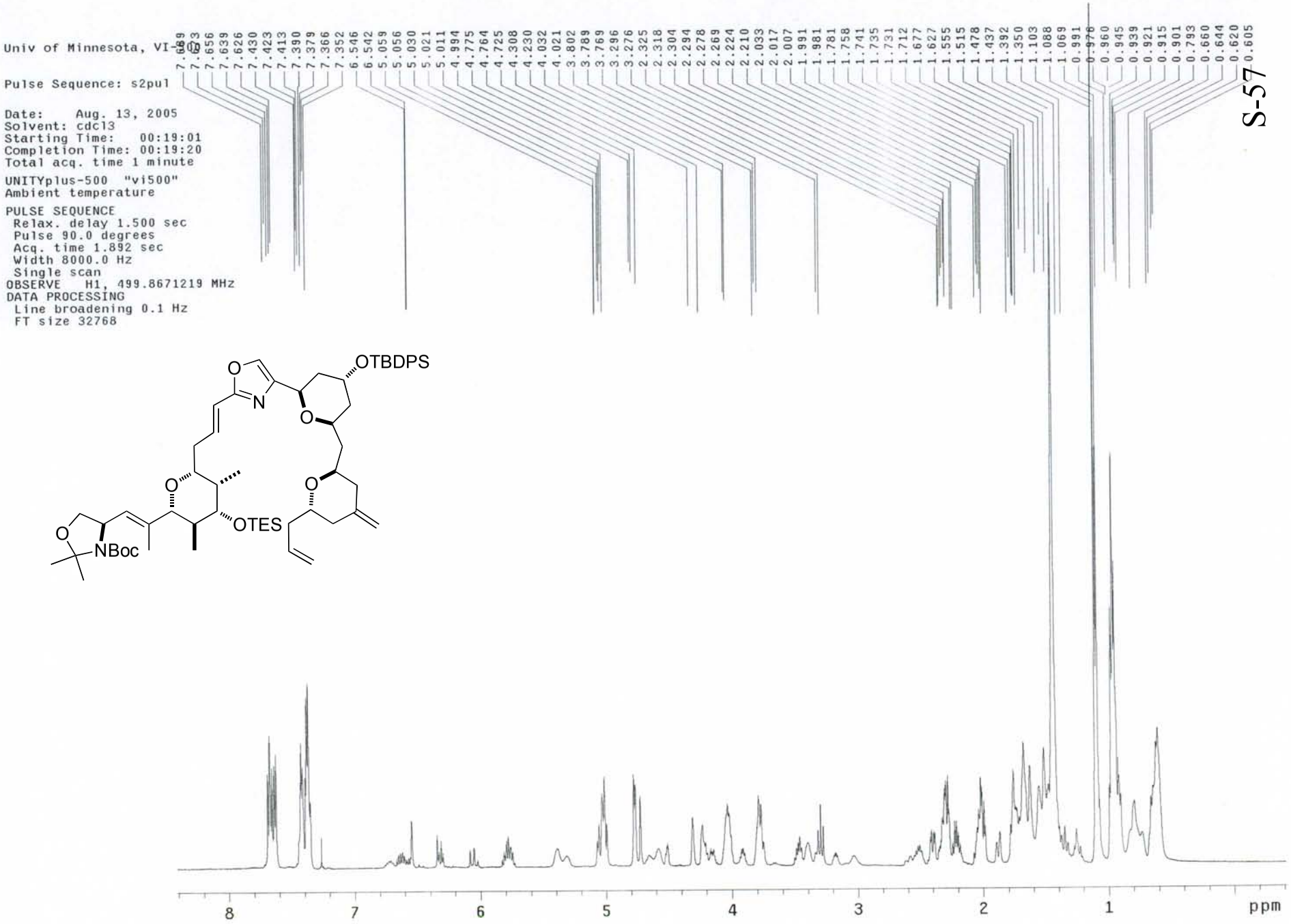

^{13}C NMR spectrum for compound **21**



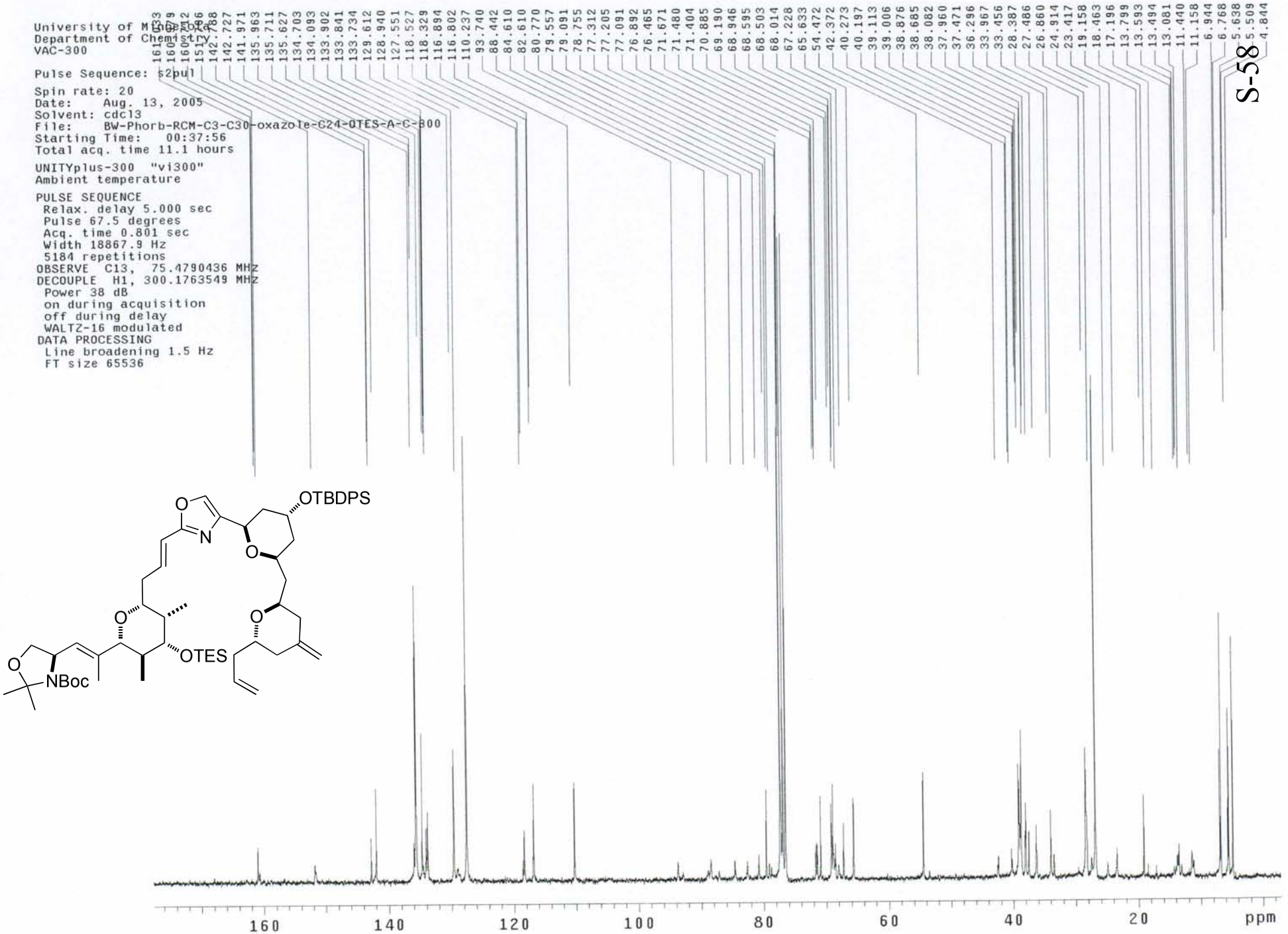
^{1}H NMR spectrum for compound **23**



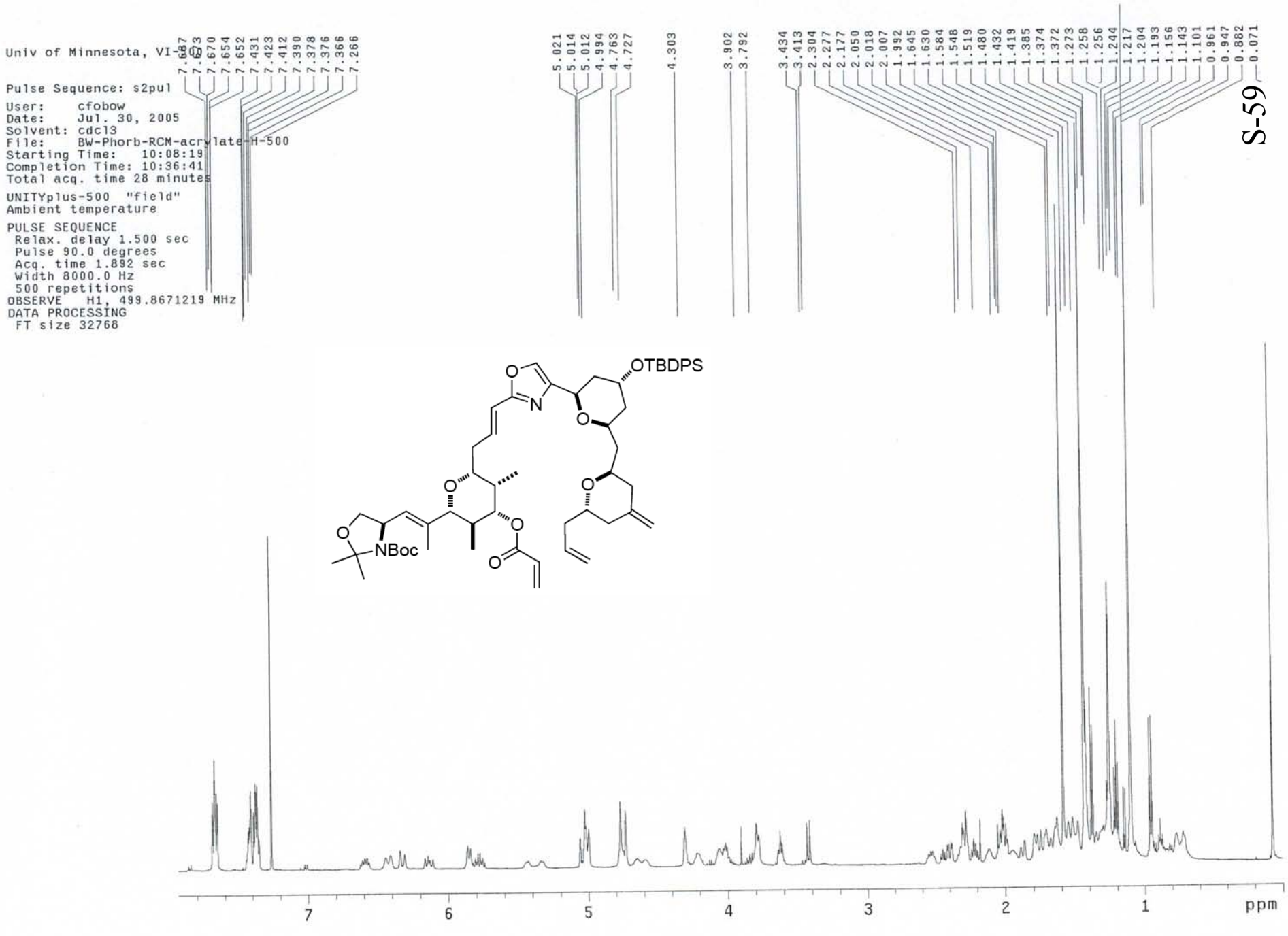
^{13}C NMR spectrum for compound **23**



^{1}H NMR spectrum for compound **24**

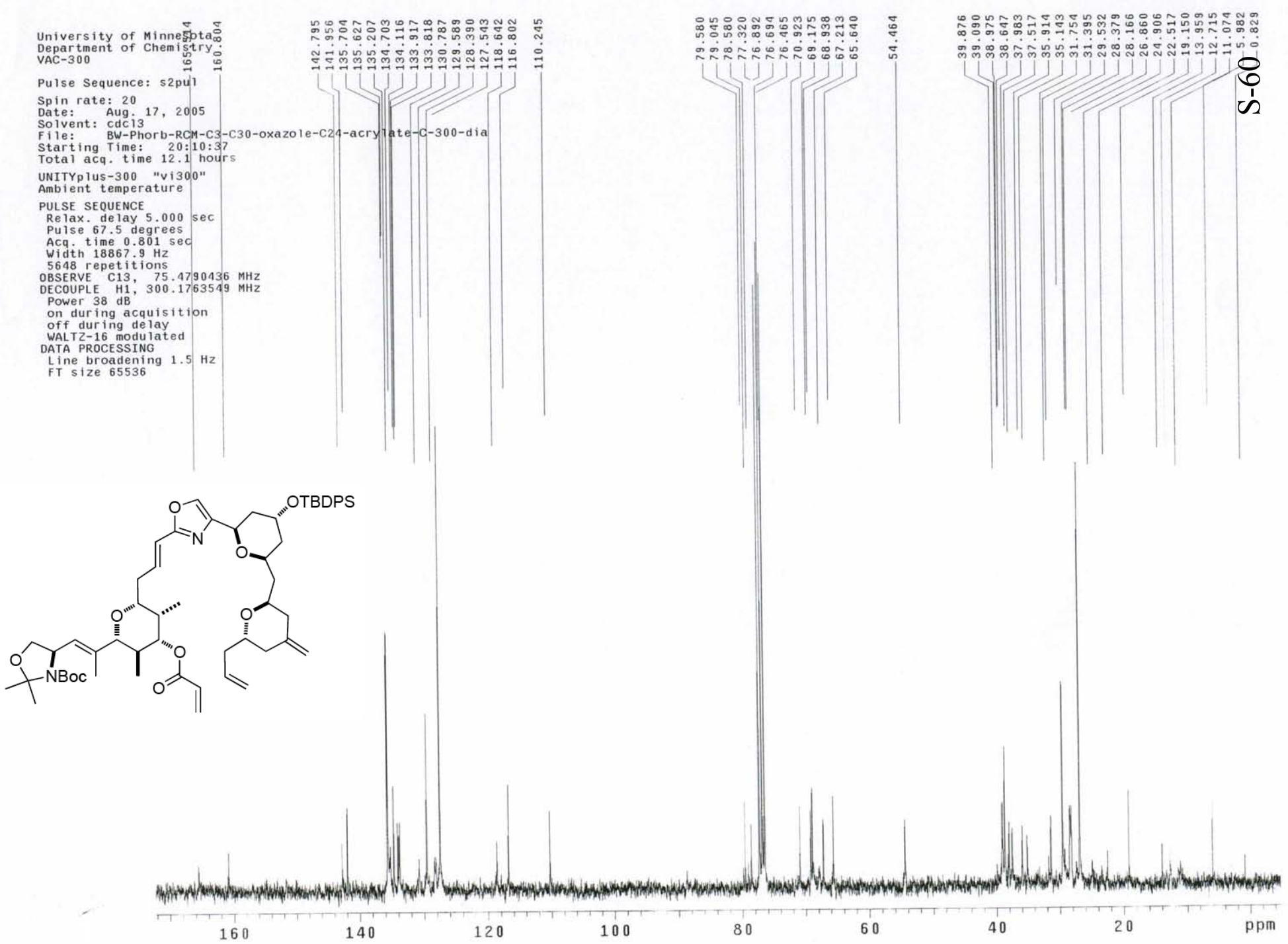


^{13}C NMR spectrum for compound **24**

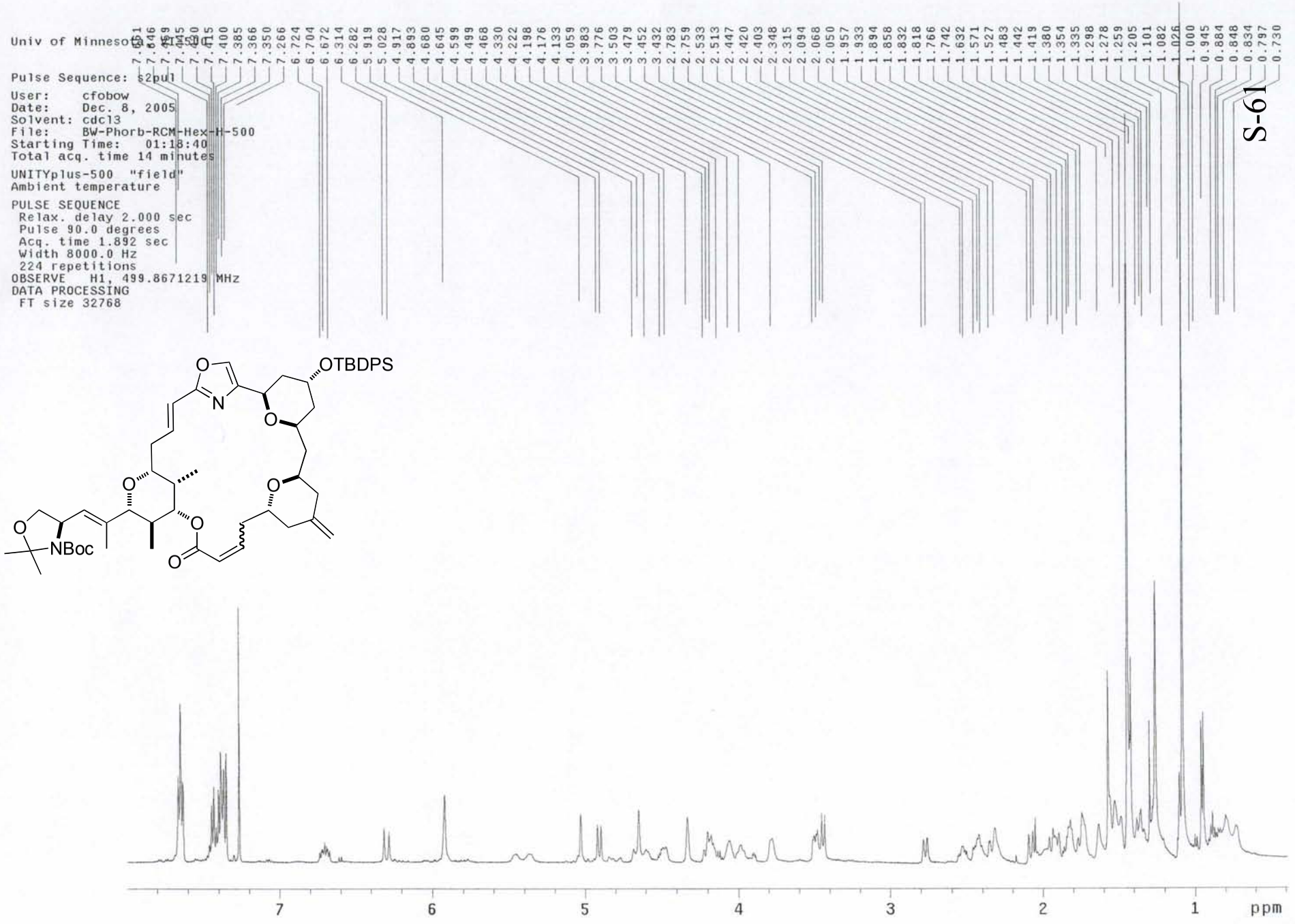


S-59

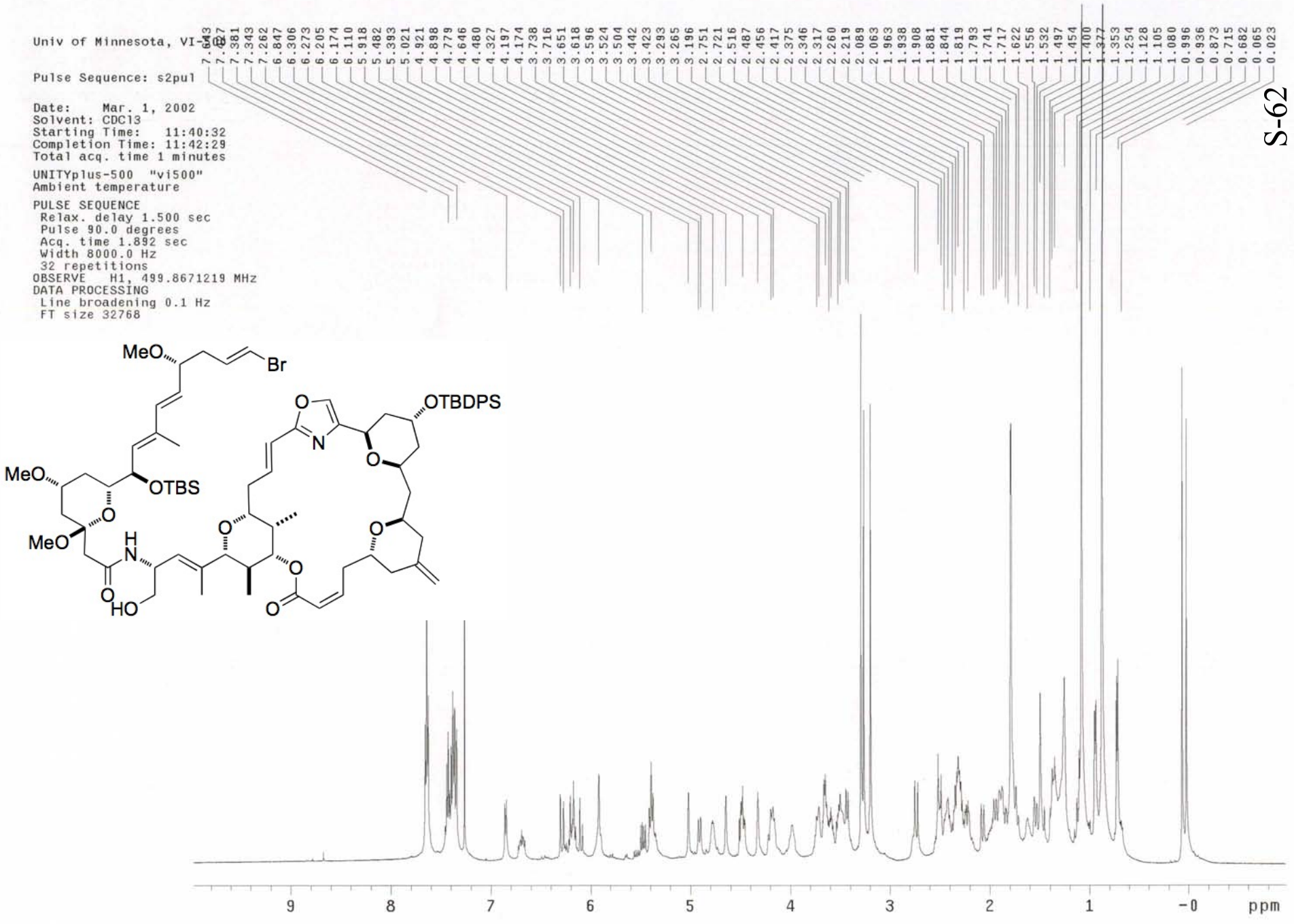
^{1}H NMR spectrum for compound **19**



^{13}C NMR spectrum for compound **19**



^{1}H NMR spectrum for the mixture of compound **14** and **15** (**14** : **15** > 10 :1)



^{1}H NMR spectrum for compound **26**

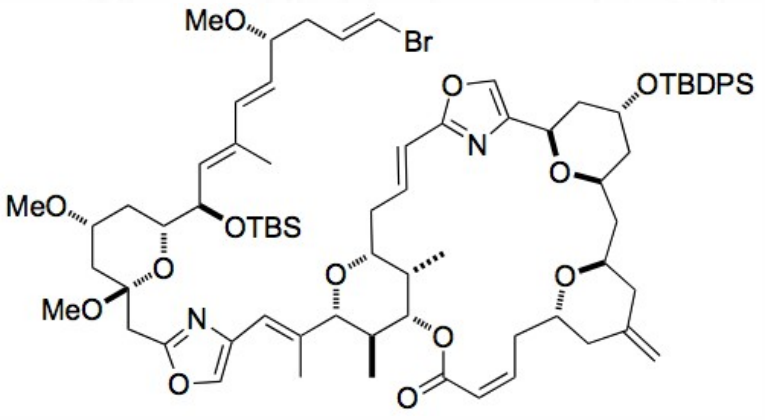
Univ of Minnesota, VI-500

Pulse Sequence: s2pul

Date: Mar. 22, 2002
Solvent: CDCl3
Starting Time: 18:42:02
Completion Time: 18:42:24
Total acq. time 1 minute

UNITYplus-500 "vi500"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
4 repetitions
OBSERVE H1, 499.8671219 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768



^{1}H NMR spectrum for compound **27**

Natural oxazole

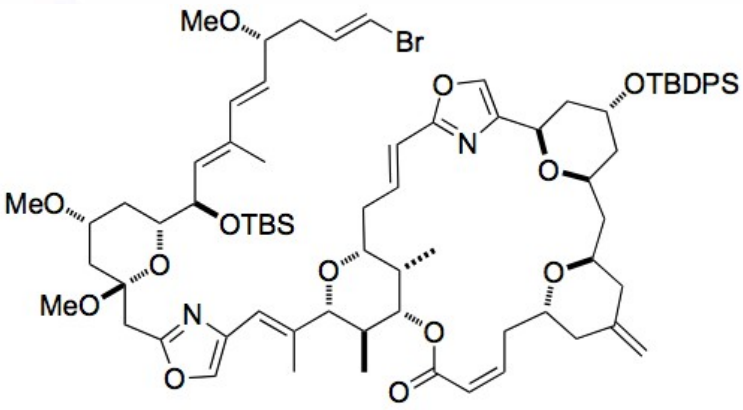
University of Minnesota
Department of Chemistry
VAC-300

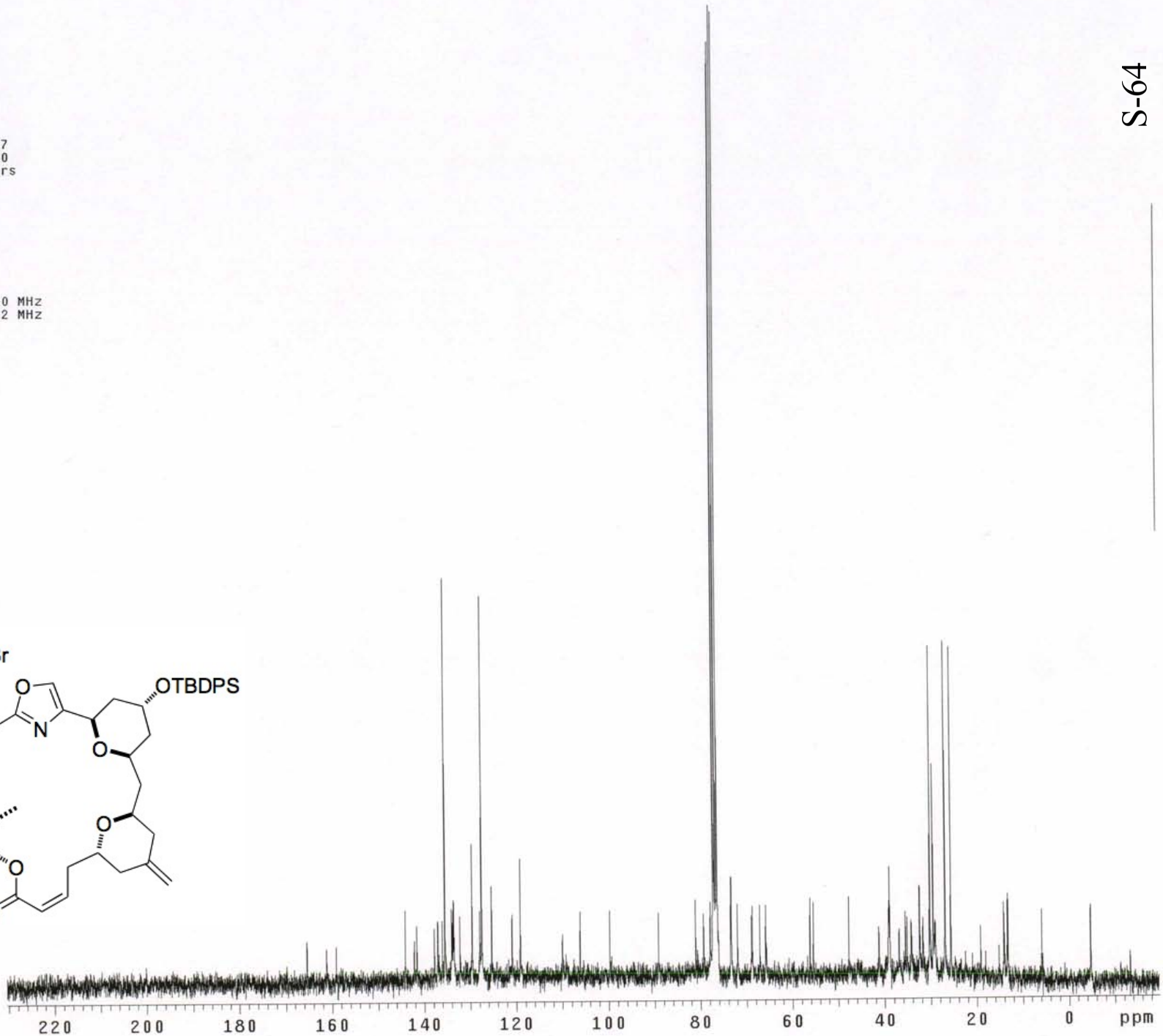
Pulse Sequence: s2pul

Spin rate: 20
Date: Mar. 22, 2002
Solvent: CDCl3
Starting Time: 19:14:07
Completion Time: 15:26:40
Total acq. time 20.2 hours

UNITYplus-300 "vxr300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18867.9 Hz
25936 repetitions
OBSERVE C13, 75.3995910 MHz
DECOUPLE H1, 299.8604072 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536





^{13}C NMR spectrum for compound **27**

45,46 · CZ9 · Amide

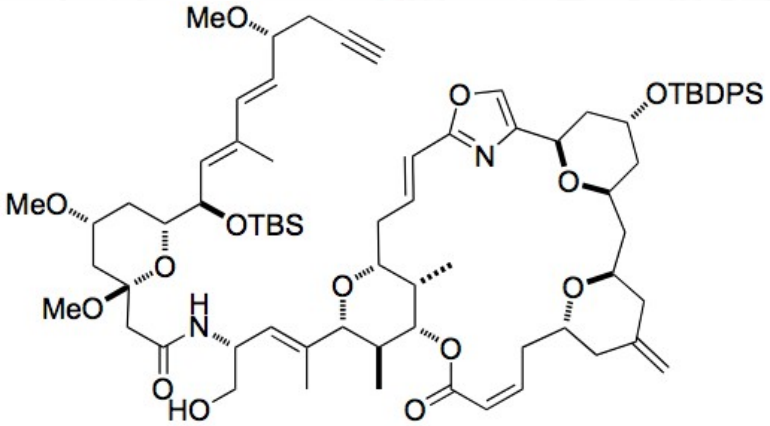
Univ of Minnesota, VI-500

Pulse Sequence: s2pul

Date: Mar. 18, 2002
Solvent: CDCl3
Starting Time: 17:32:46
Completion Time: 17:36:31
Total acq. time 3 minutes

UNITYplus-500 "vi500"
Ambient temperature

PULSE SEQUENCE
Relax. delay 1.500 sec
Pulse 90.0 degrees
Acq. time 1.892 sec
Width 8000.0 Hz
64 repetitions
OBSERVE H1, 499.8671219 MHz
DATA PROCESSING
Line broadening 0.1 Hz
FT size 32768



^{1}H NMR spectrum for compound **32**

4546 Amidecarbon

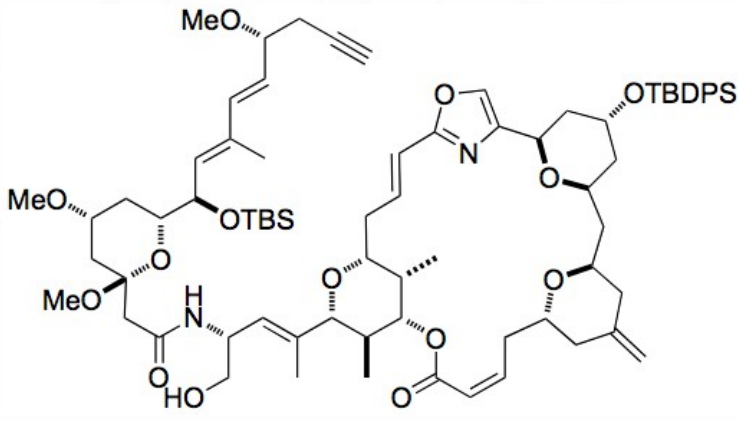
University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pul

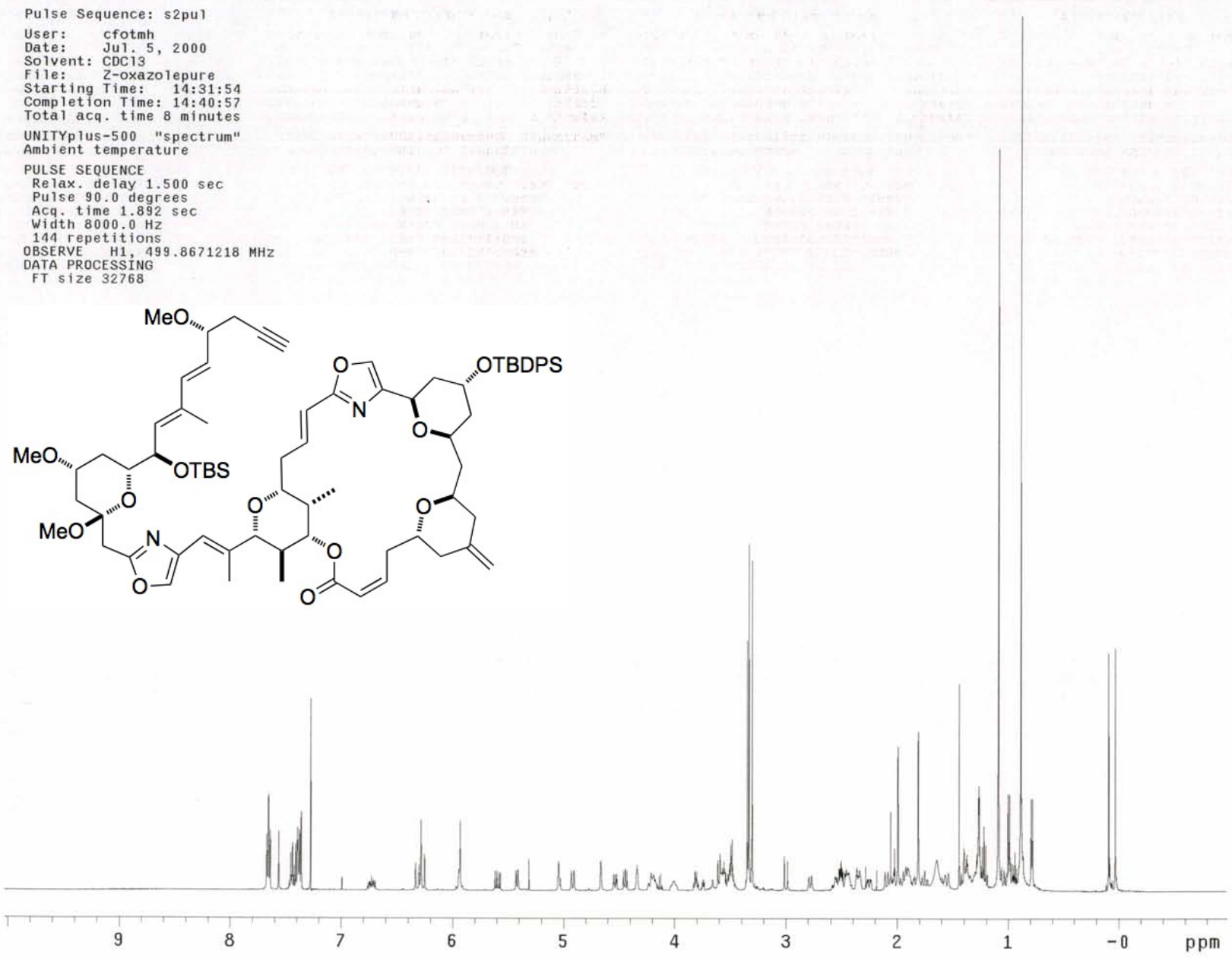
Spin rate: 20
Date: Mar. 18, 2002
Solvent: CDCl3
Starting Time: 17:54:26
Total acq. time 14.6 hours

UNITYplus-300 "vxr300"
Ambient temperature

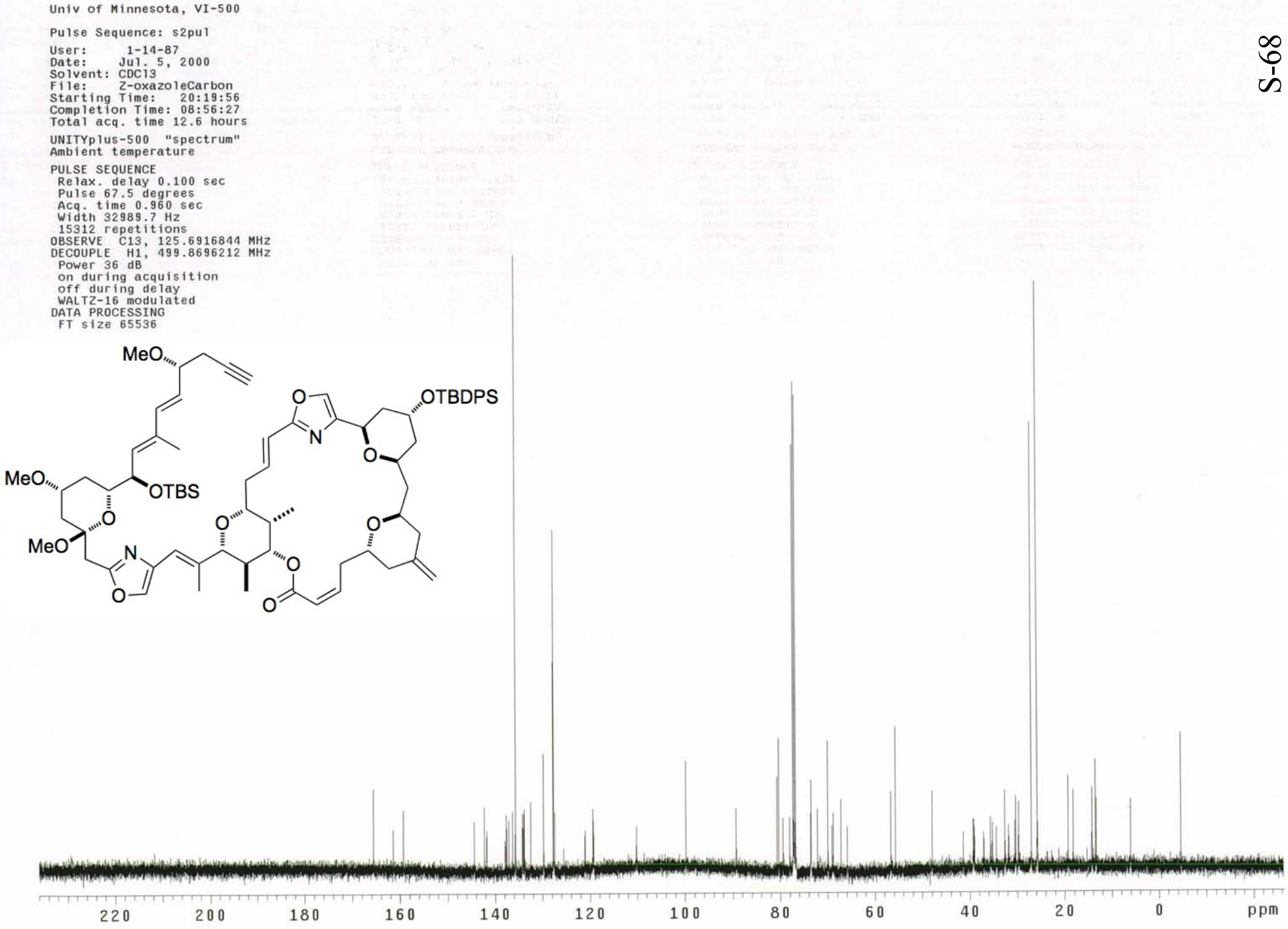
PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18867.9 Hz
18784 repetitions
OBSERVE C13, 75.3995910 MHz
DECOUPLE H1, 299.8604072 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536



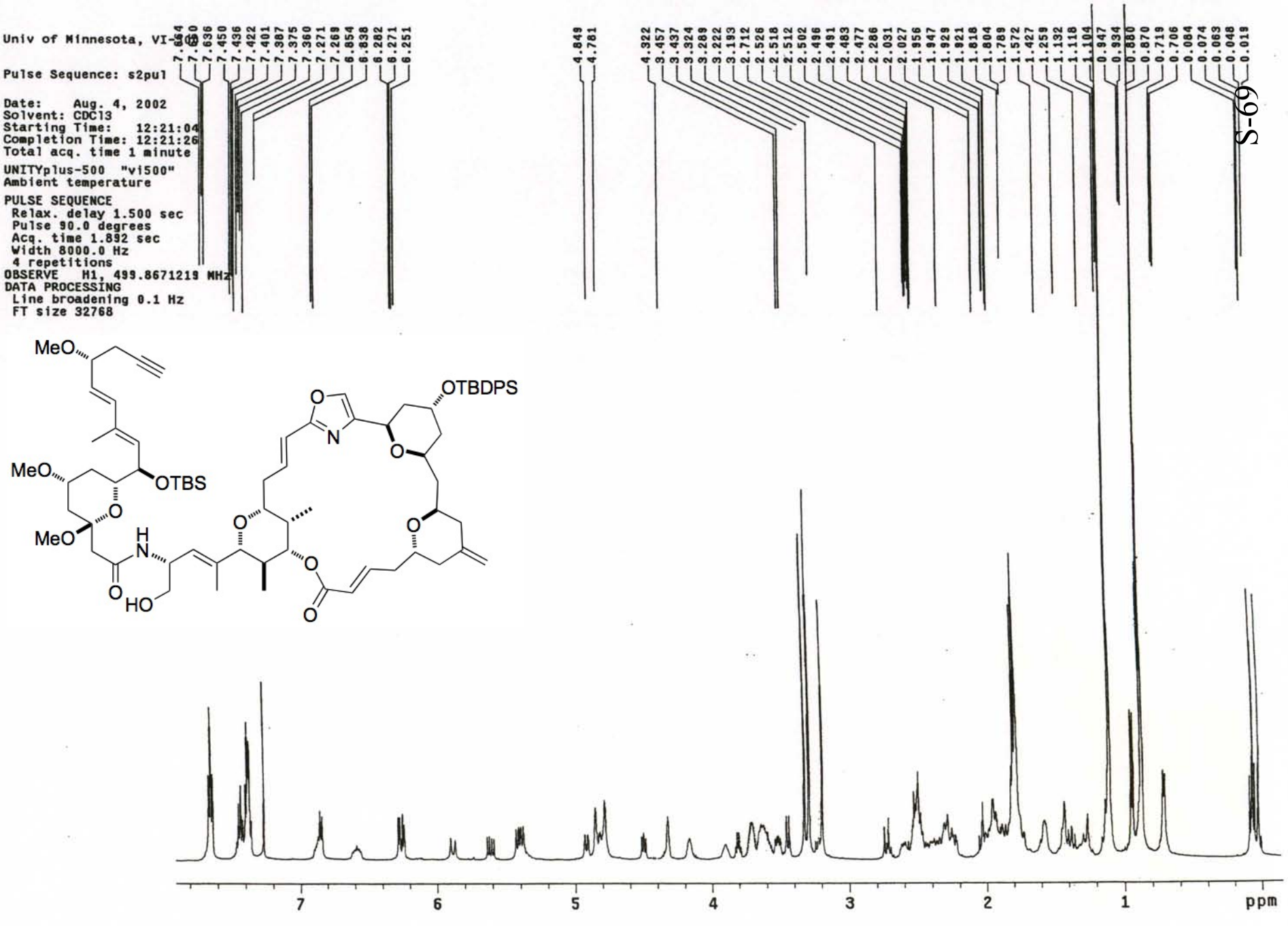
^{13}C NMR spectrum for compound **32**



^{1}H NMR spectrum for compound **33**



^{13}C NMR spectrum for compound **33**



^{1}H NMR spectrum for compound **38**

File 25AmideC

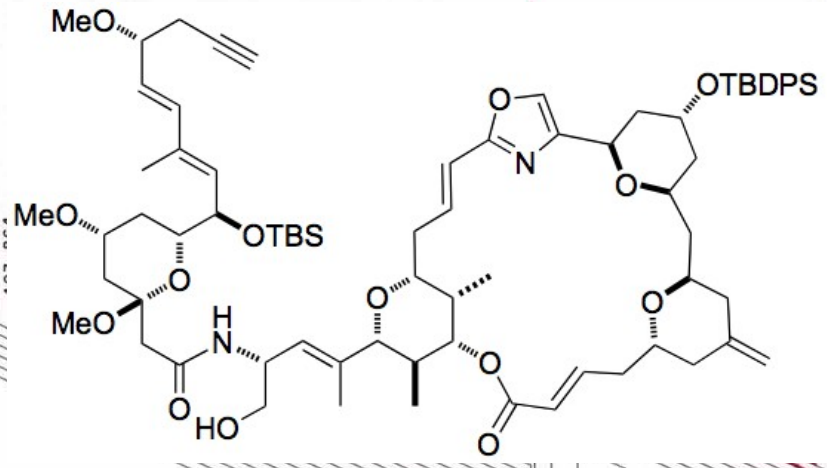
University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pul

Spin rate: 20
Date: Aug. 4, 2002
Solvent: CDCl3
Starting Time: 15:52:06
Total acq. time 17.7 hours

UNITYplus-300 "vxr300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18867.9 Hz
22784 repetitions
OBSERVE C13, 75.3995910 MHz
DECOUPLE H1, 299.8604072 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536

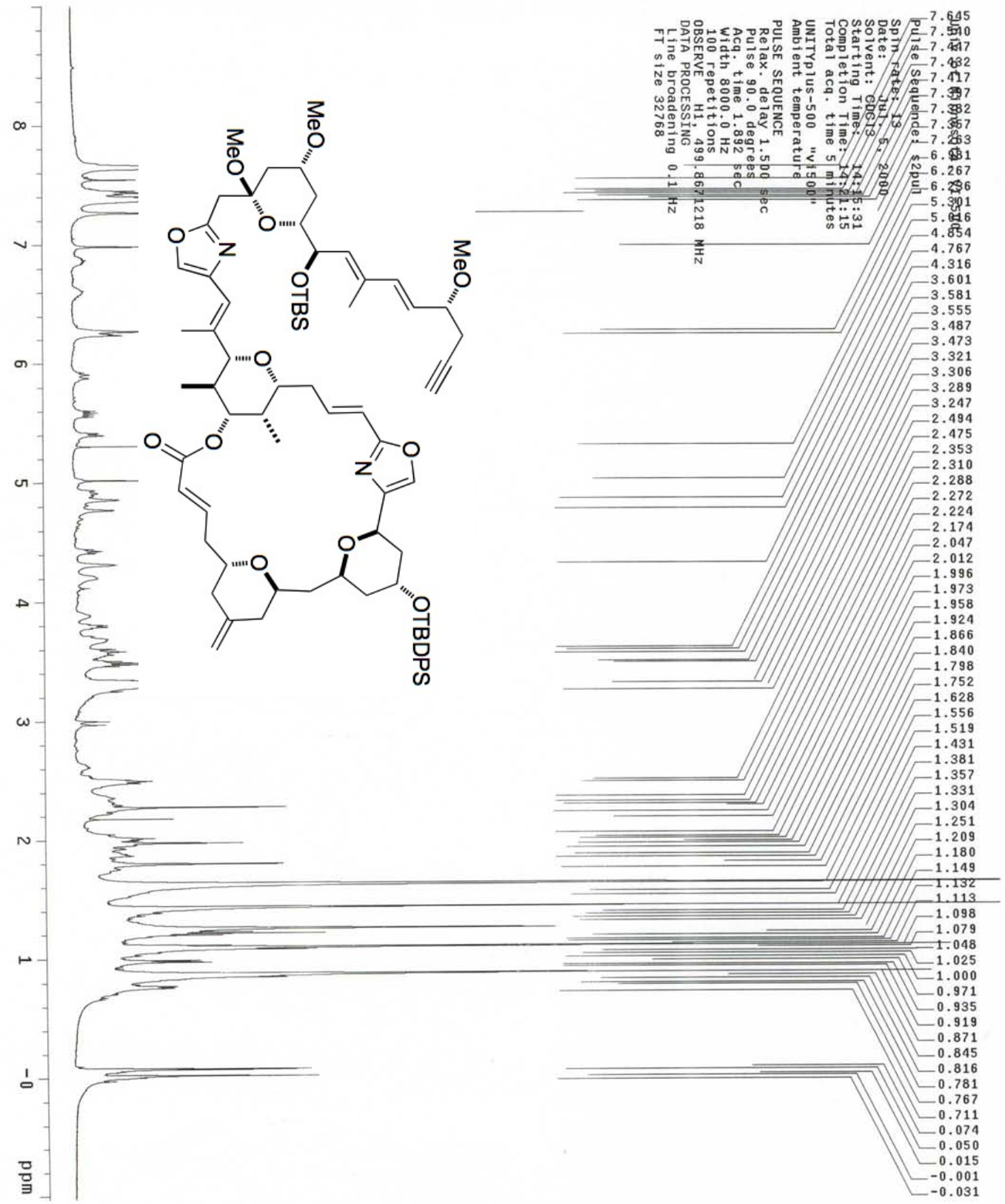


168.903
167.002
161.109
146.864
142.307
141.406

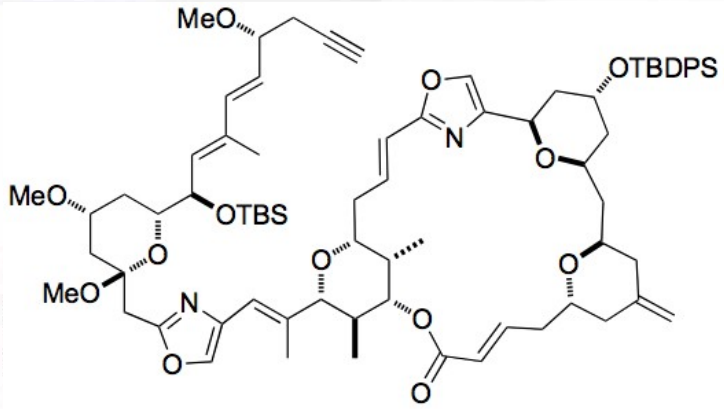
49.136
47.563
43.716
40.349
38.907
38.227
37.792
37.525
36.525
34.464
34.242
33.807
33.639
32.418
31.349
30.219
29.624
26.944
25.692
25.517
19.242
18.150
17.791
13.318
13.104
11.929
5.799
3.211
-4.515

220 200 180 160 140 120 100 80 60 40 20 0 ppm

^{13}C NMR spectrum for compound **38**



^{1}H NMR spectrum for compound **39**



68C

University of Minnesota
Department of Chemistry
VAC-300

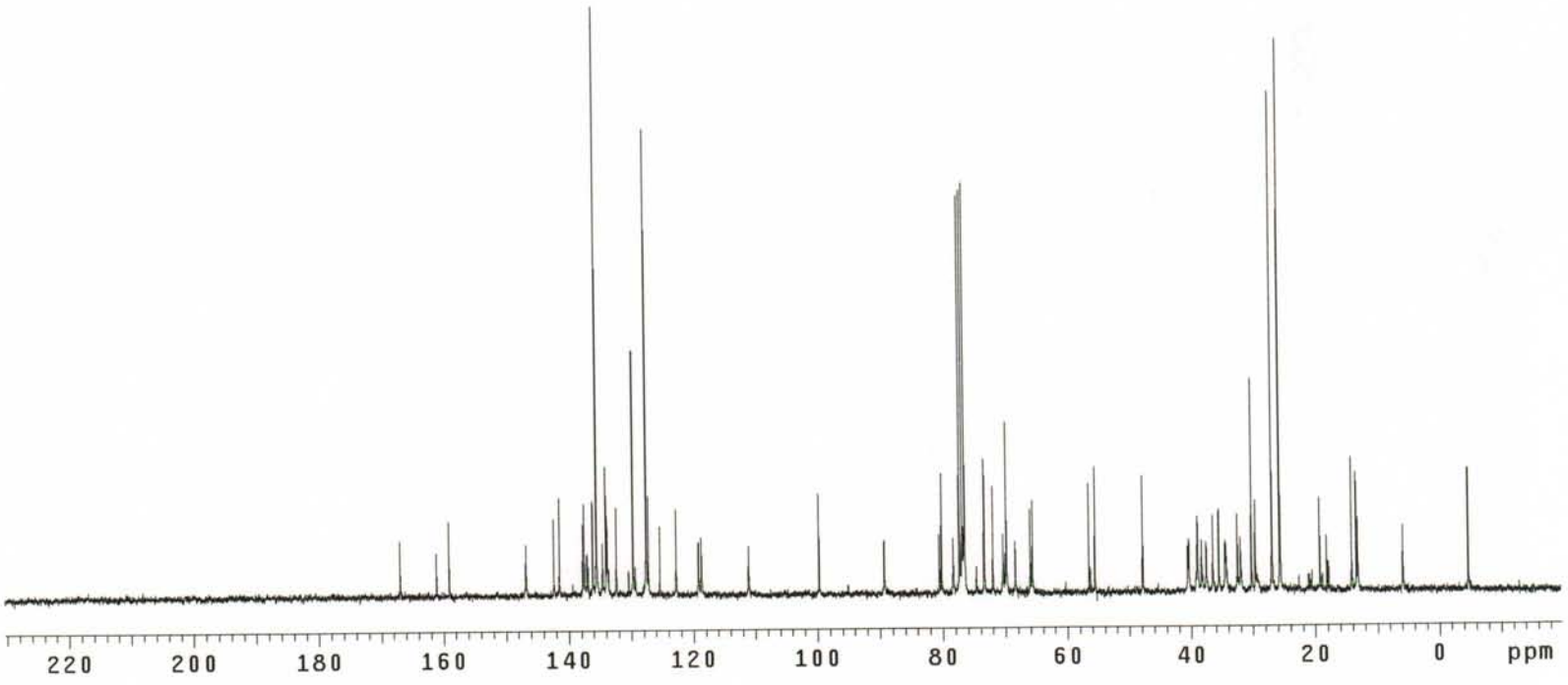
Pulse Sequence: s2pul

Spin rate: 20
Date: Aug. 22, 2002
Solvent: CDCl3
Starting Time: 23:34:50
Total acq. time 10.1 hours

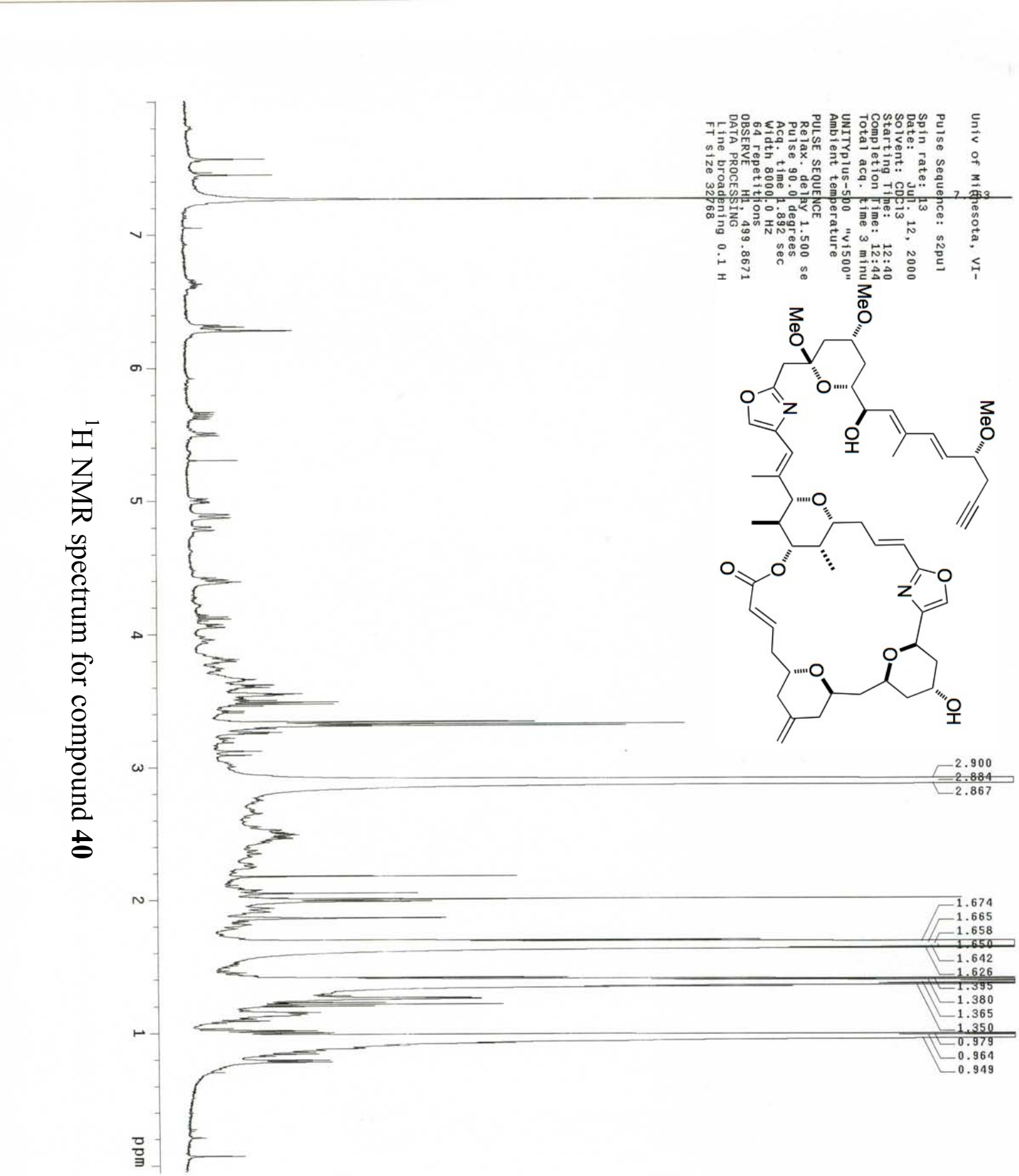
UNITYplus-300 "vxr300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18867.9 Hz
12992 repetitions
OBSERVE C13, 75.3995910 MHz
DECOUPLE H1, 299.8604072 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536

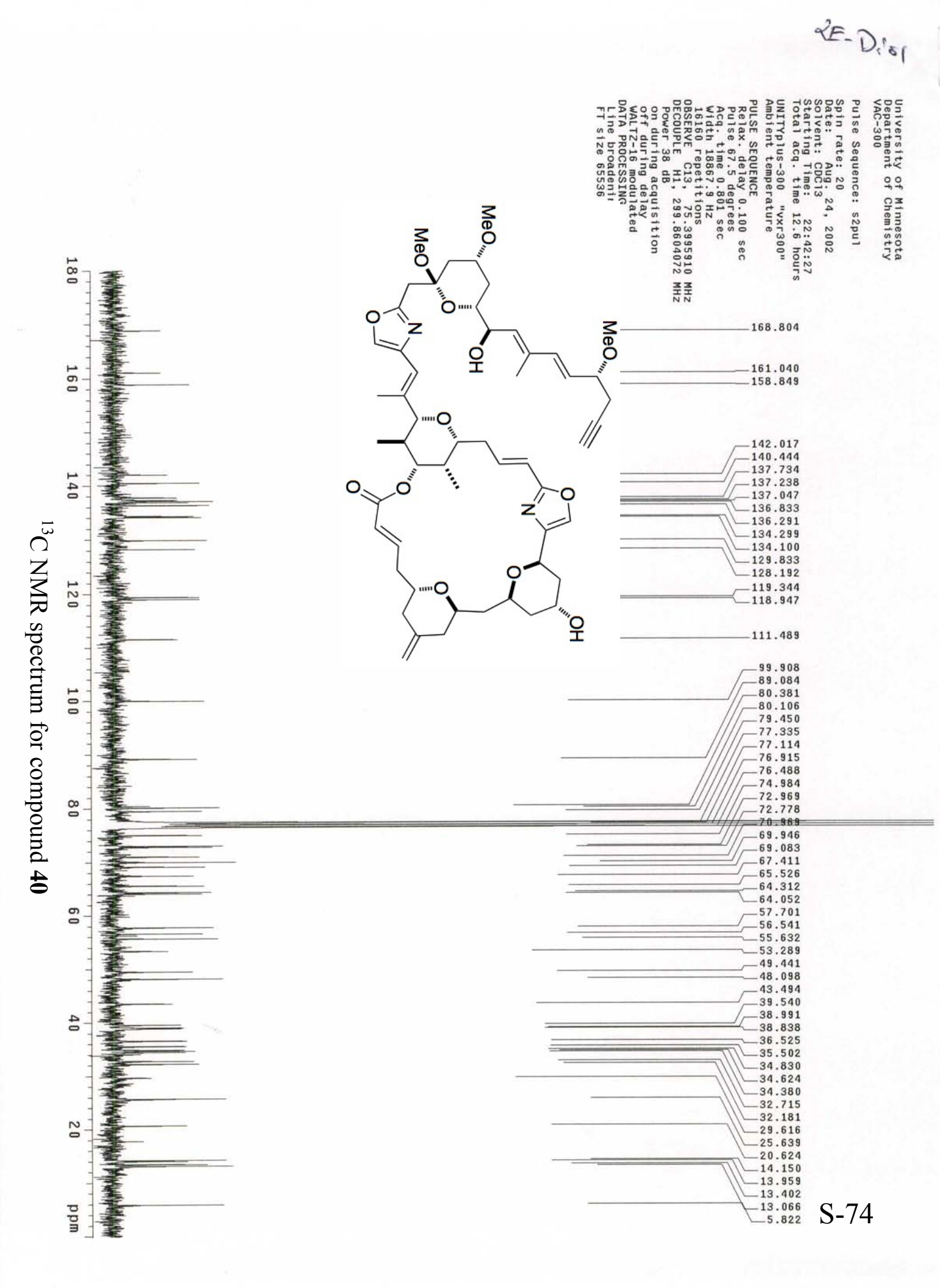
72.007
70.366
70.098
69.854
68.419
66.022
65.655
56.510
55.556
47.907
47.823
40.533
40.342
38.998
38.922
38.281
37.517
36.464
35.487
34.471
34.303
32.494
31.983
30.227
29.616
26.944
25.692
25.631
19.249
18.143
14.150
13.387
13.142
5.883
-4.652
-4.706



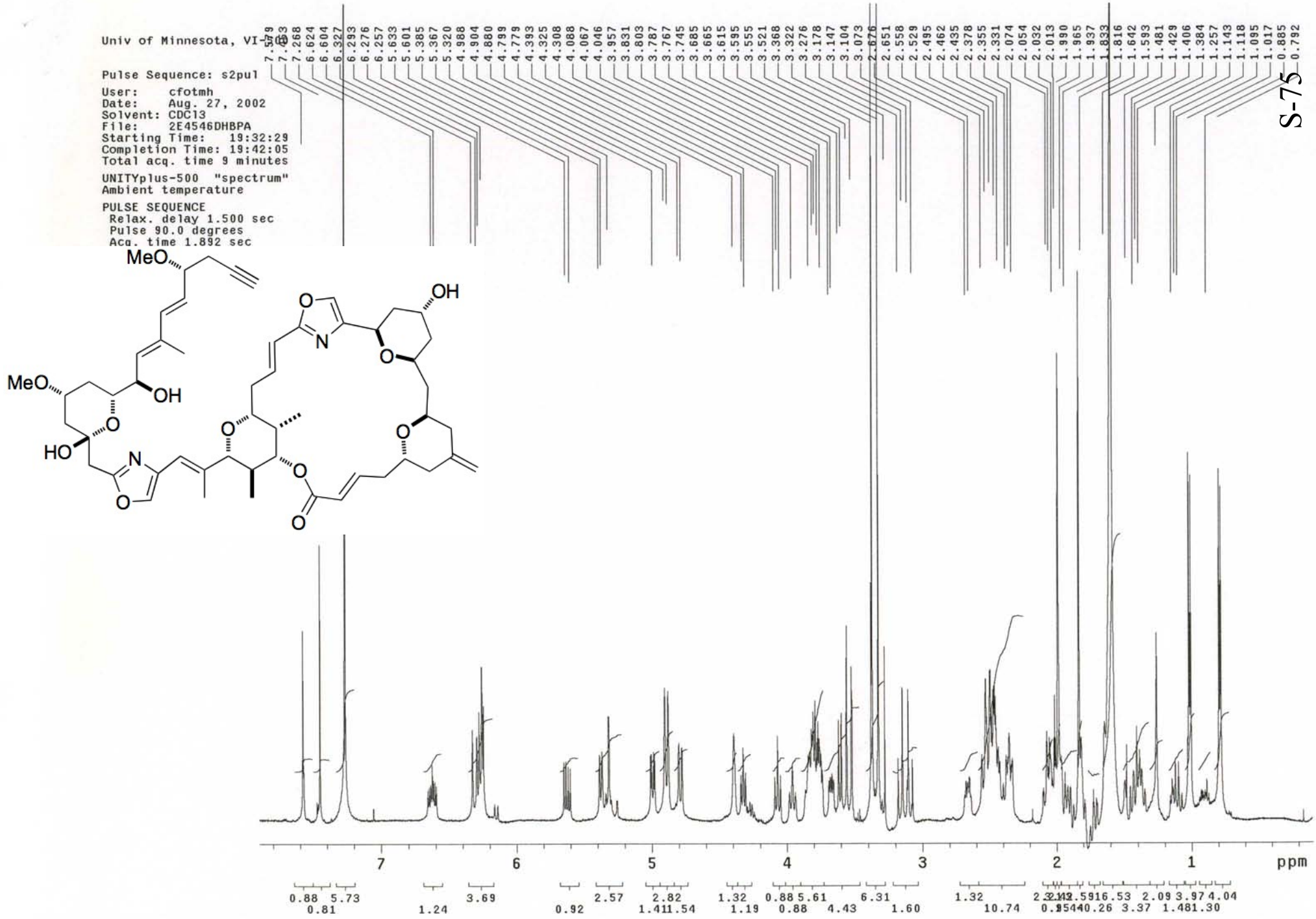
^{13}C NMR spectrum for compound **39**



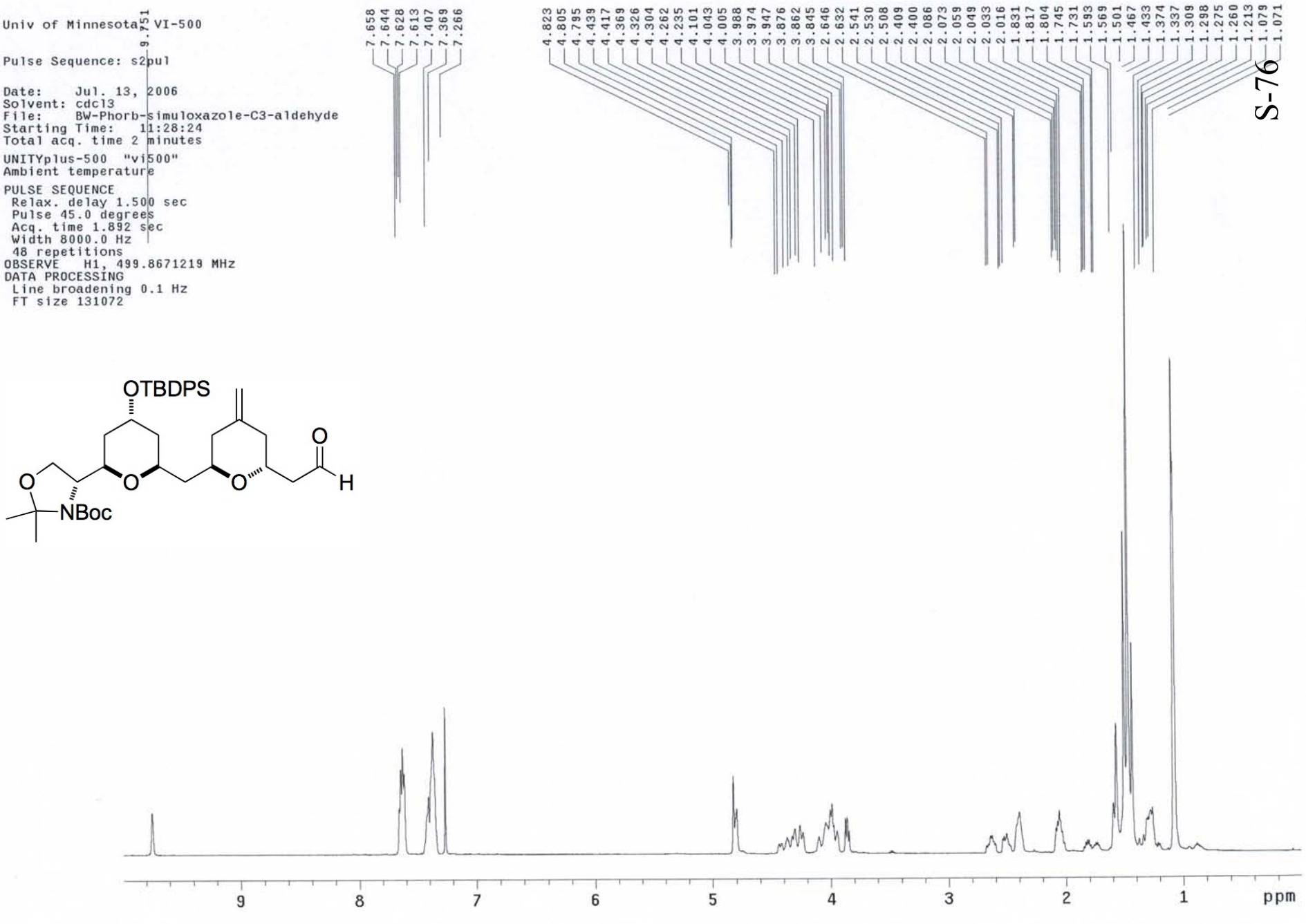
^{1}H NMR spectrum for compound **40**



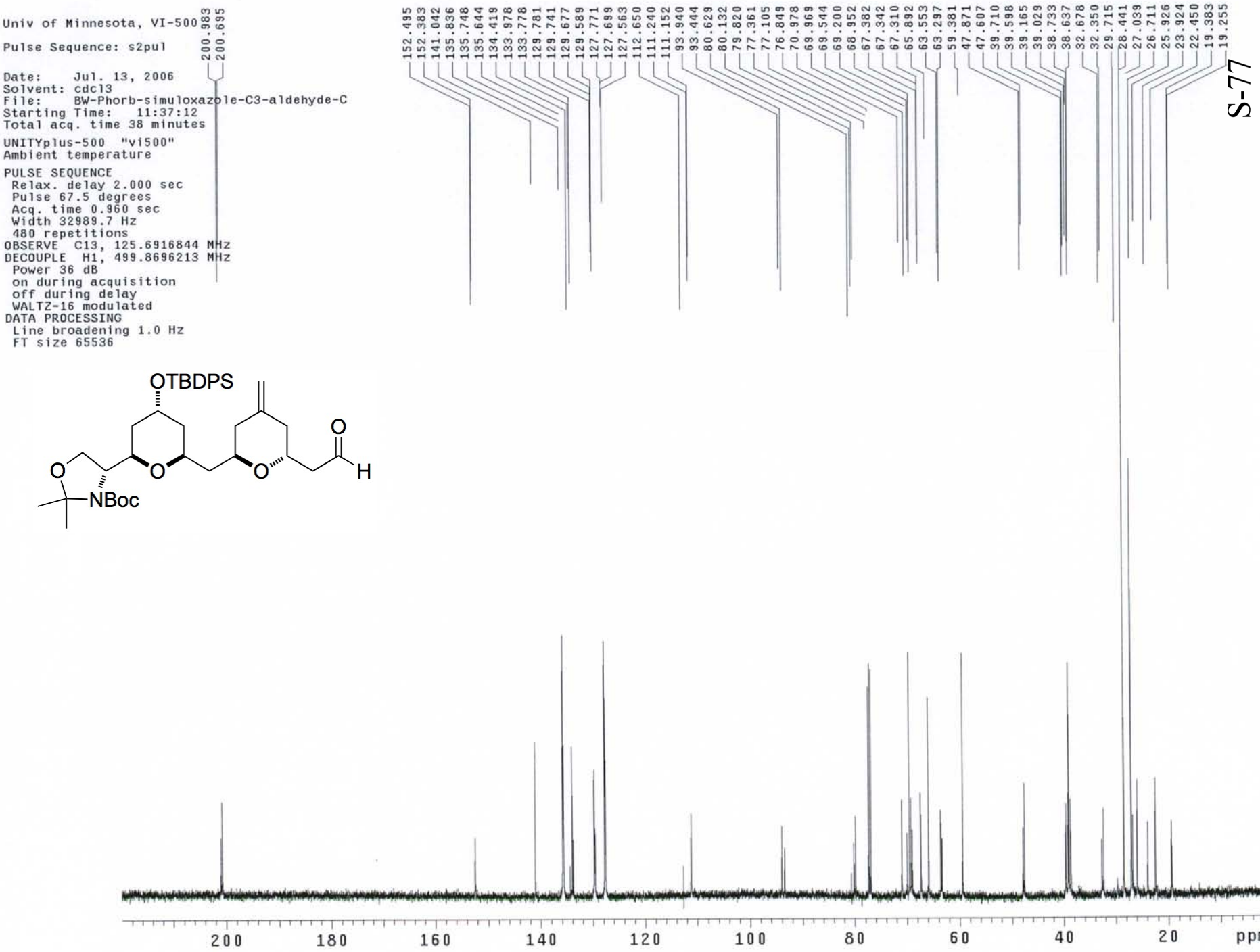
^{13}C NMR spectrum for compound **40**



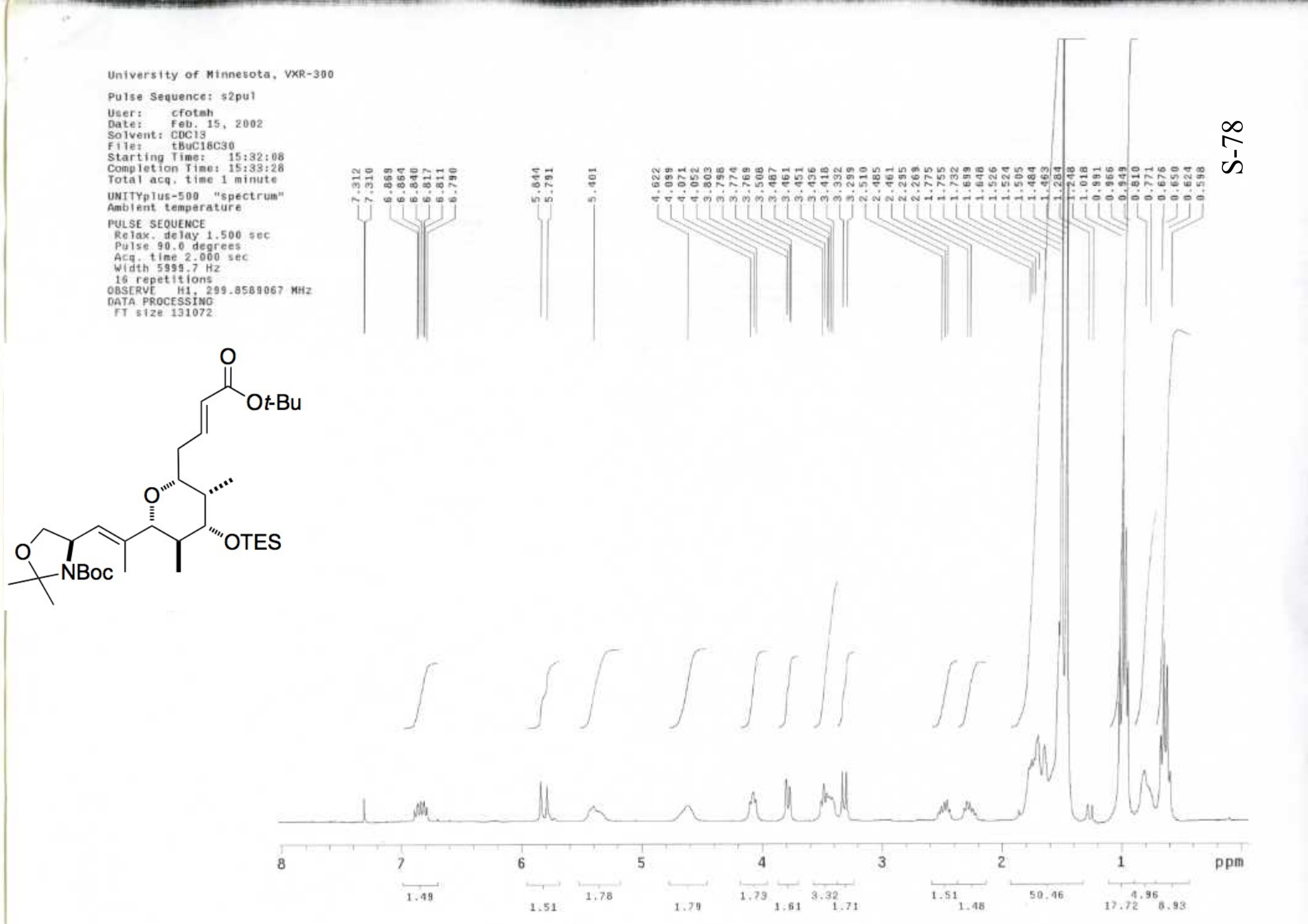
^{1}H NMR spectrum for compound **41**



^{1}H NMR spectrum for compound **52**



^{13}C NMR spectrum for compound **52**



^{1}H NMR spectrum for compound **48**

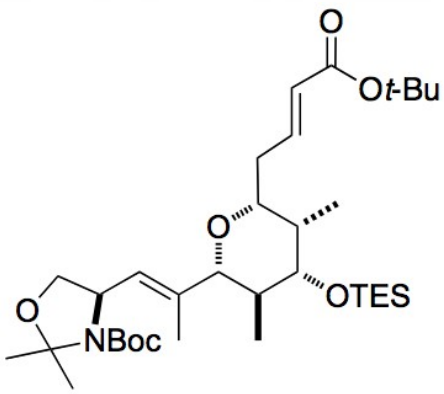
University of Minnesota
Department of Chemistry
VAC-300

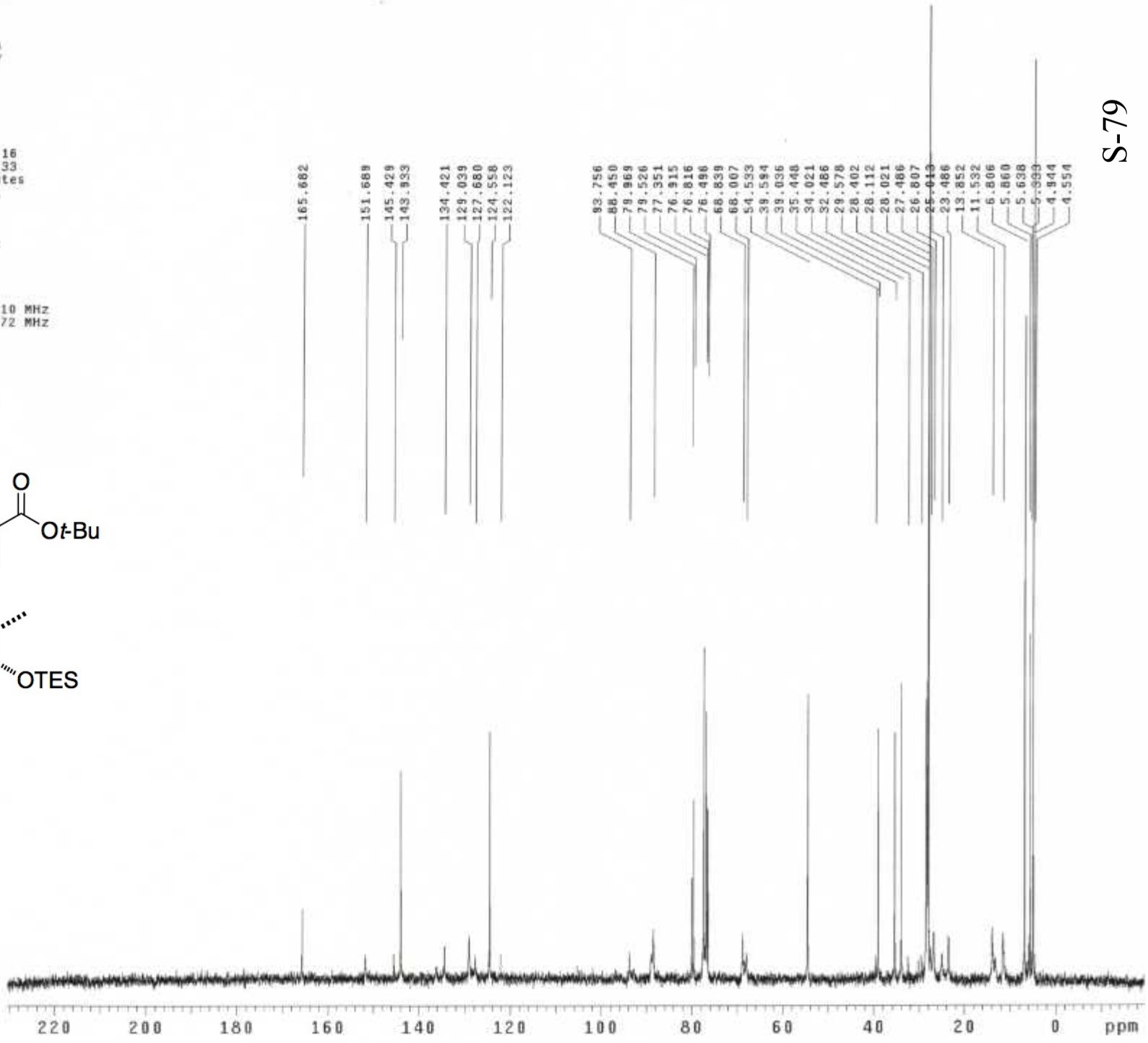
Pulse Sequence: s2pul

Spin rate: 20
Date: Feb. 15, 2002
Solvent: CDCl3
Starting Time: 15:35:16
Completion Time: 16:02:33
Total acq. time 26 minutes

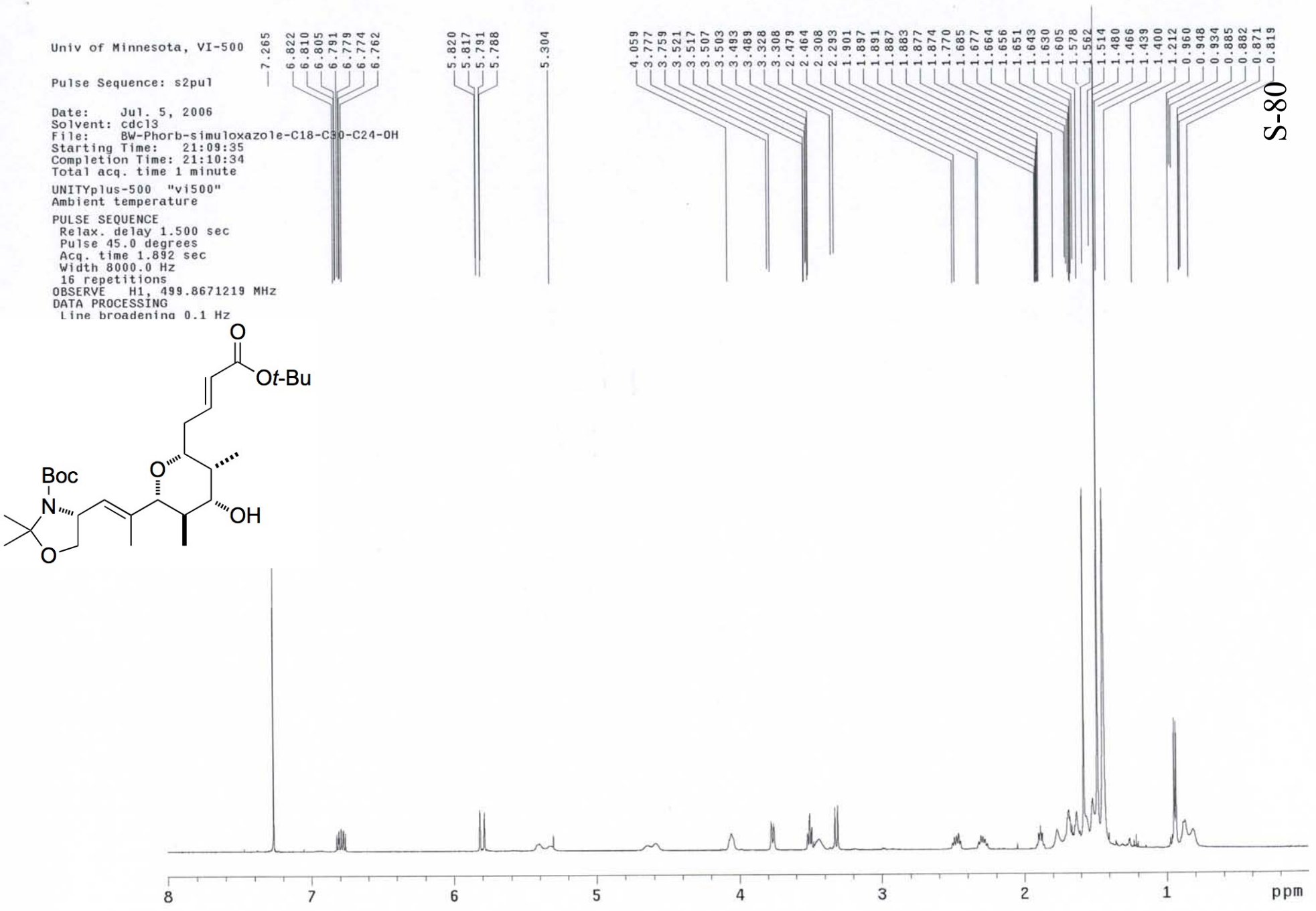
UNITYplus-300 "vxr300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18867.9 Hz
576 repetitions
OBSERVE C13, 75.3995910 MHz
DECOUPLE H1, 299.8604072 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536

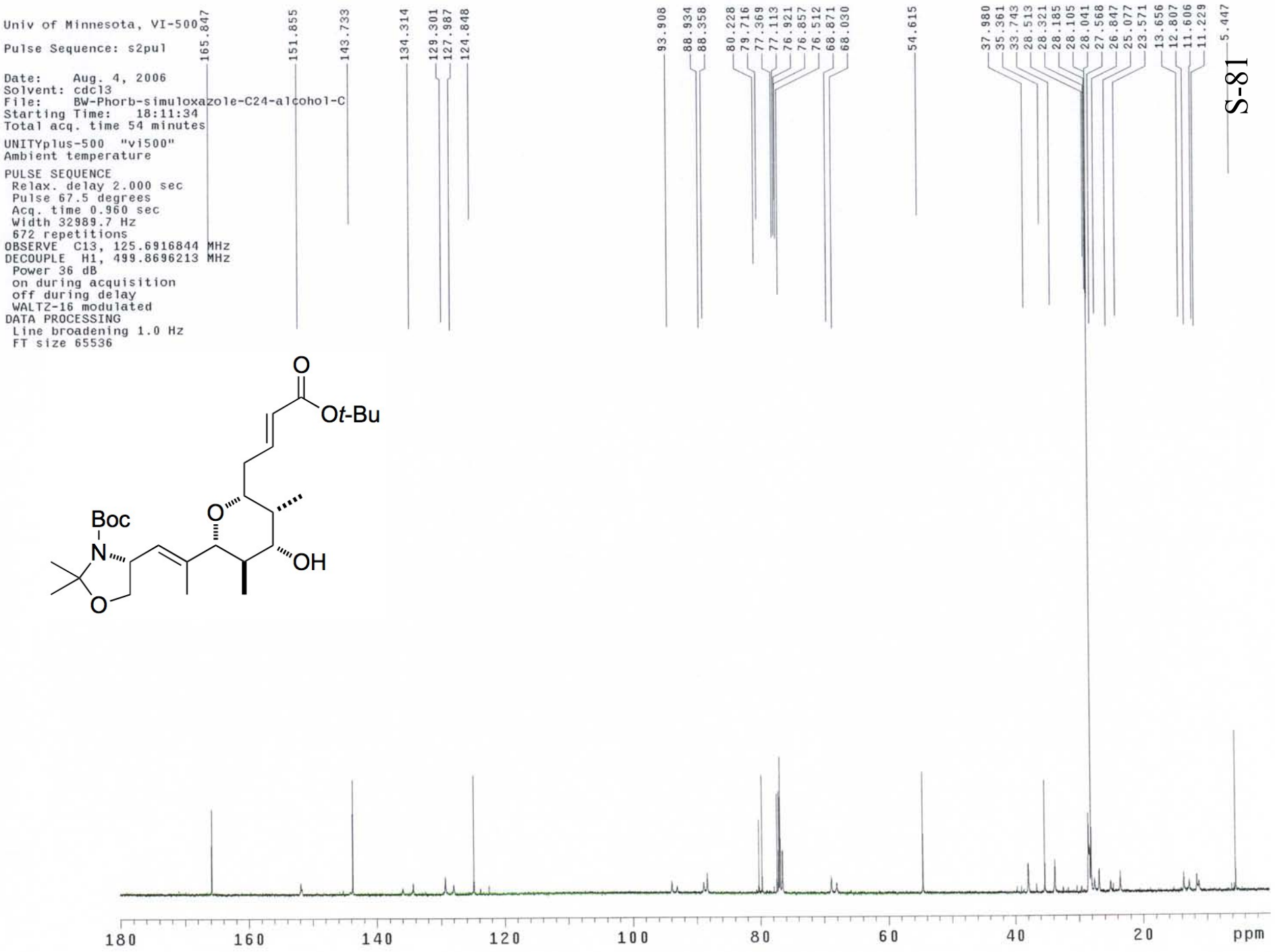




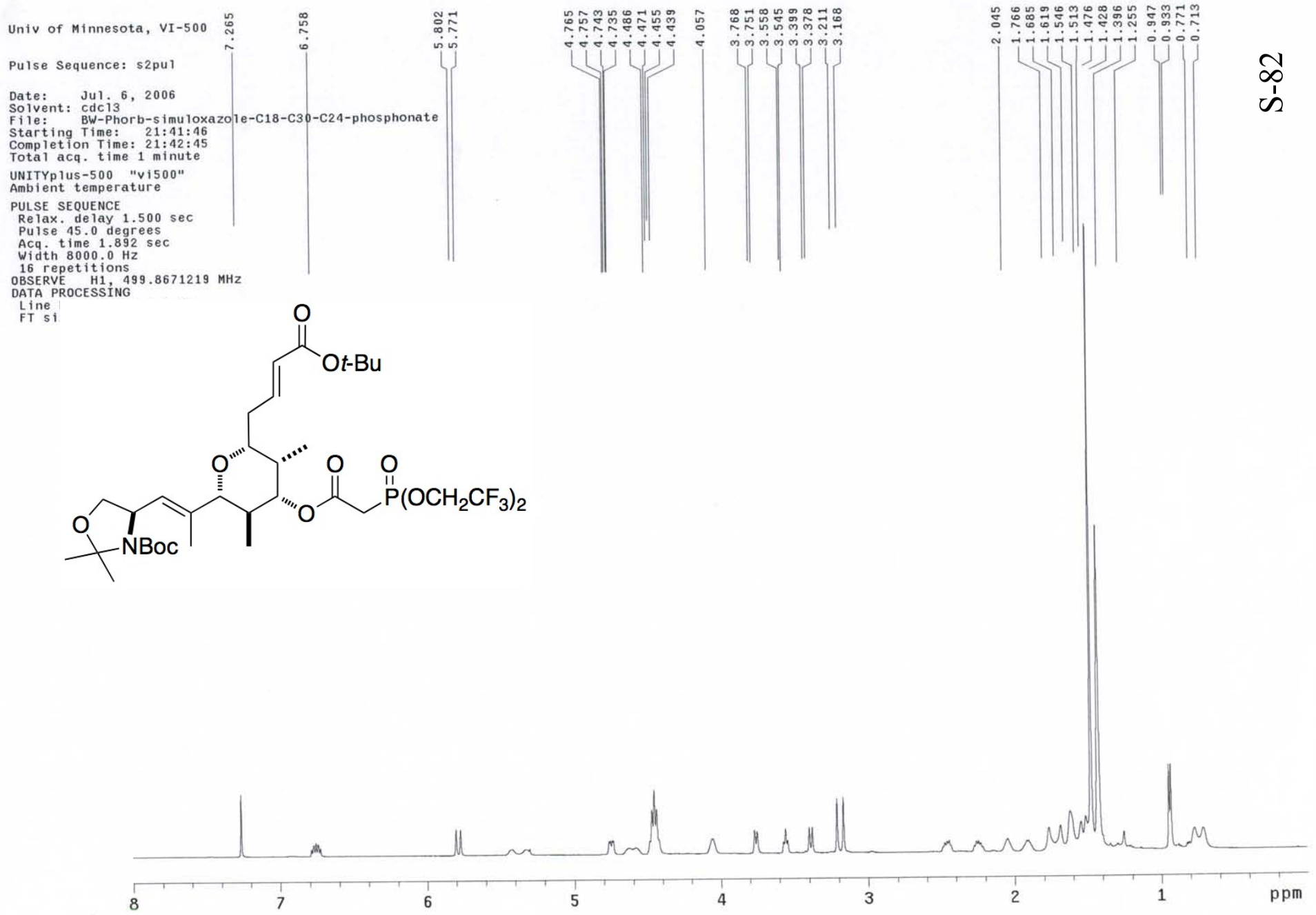
^{13}C NMR spectrum for compound **48**



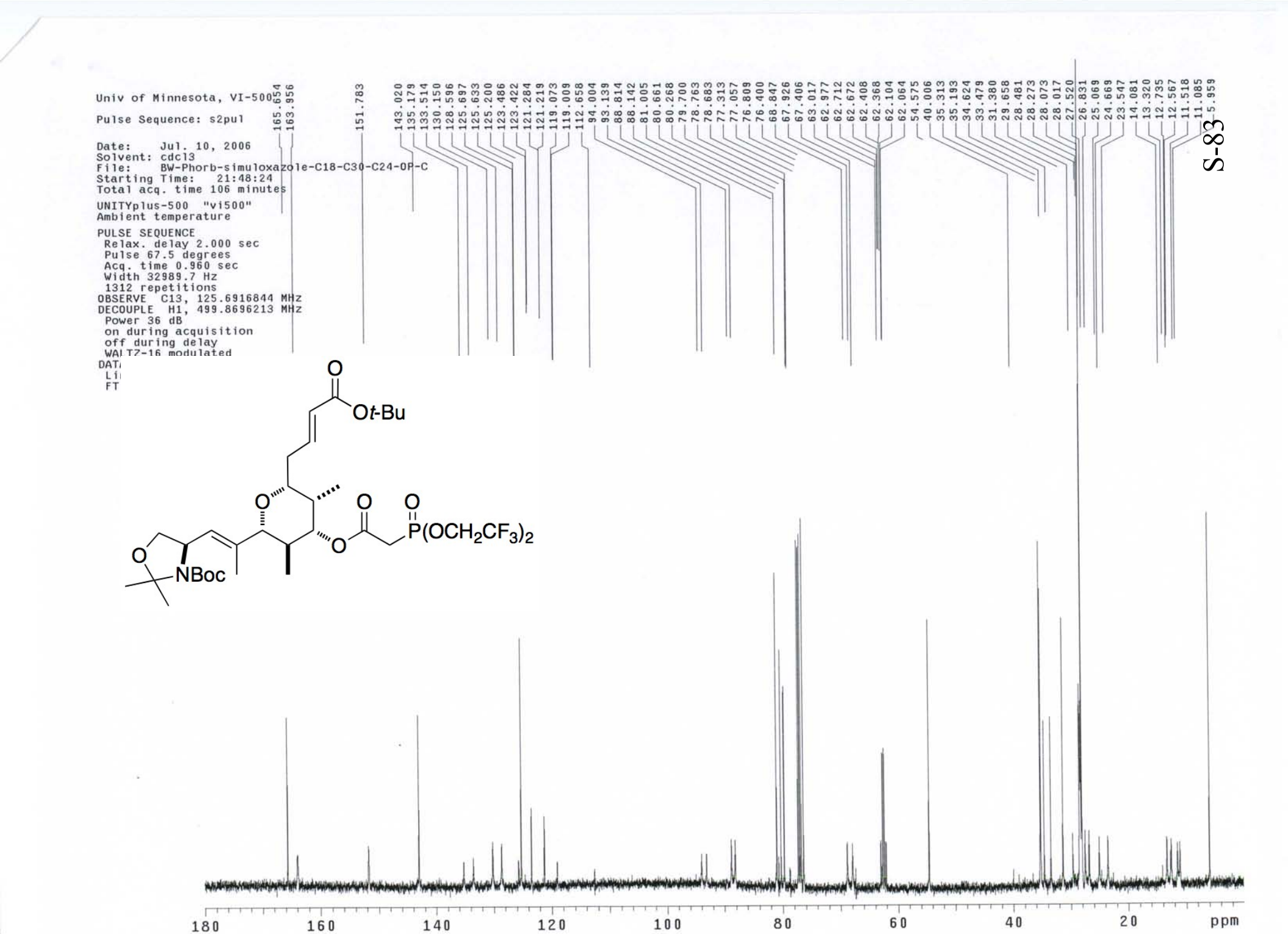
^{1}H NMR spectrum for compound **53**



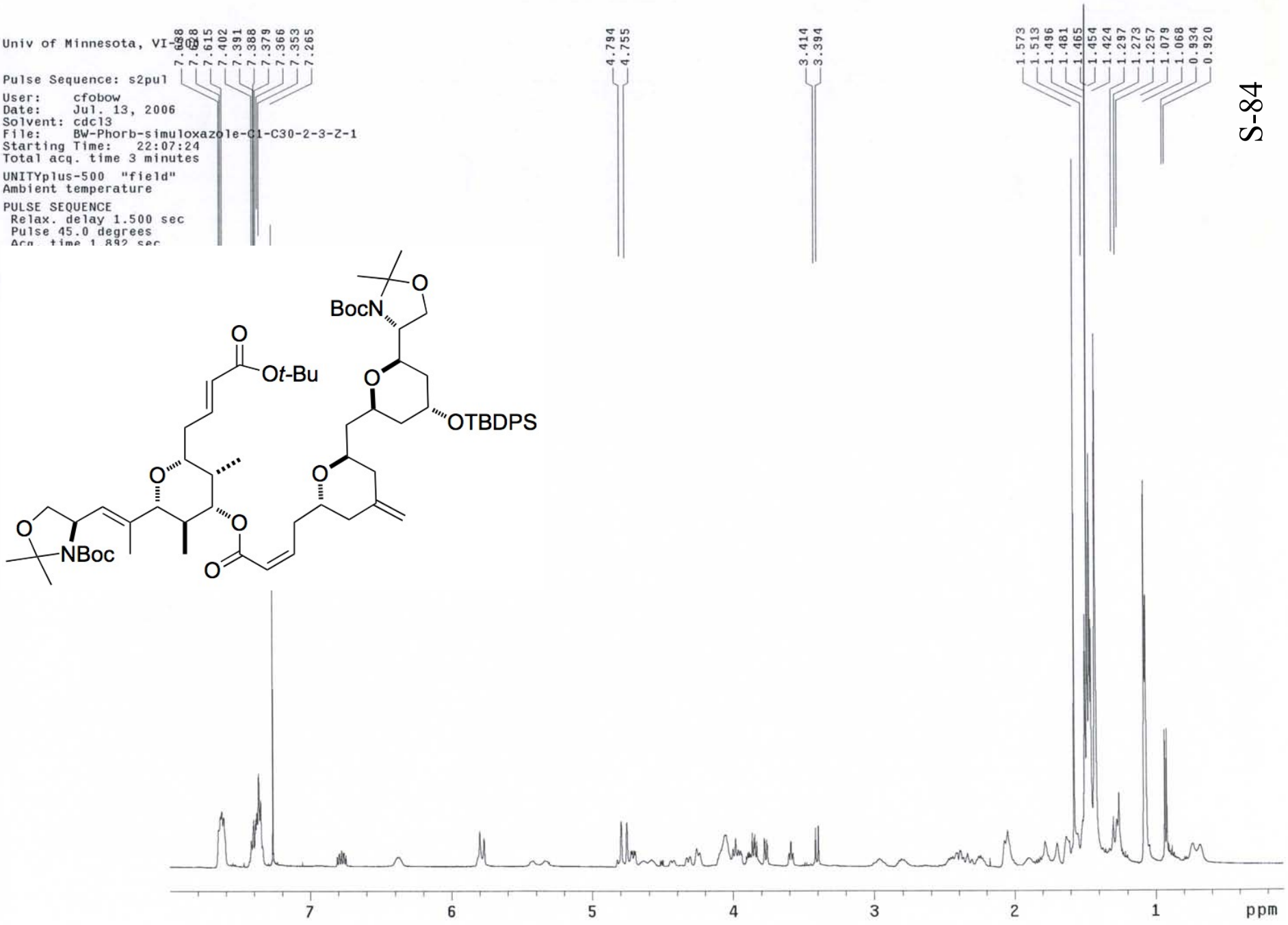
^{13}C NMR spectrum for compound **53**



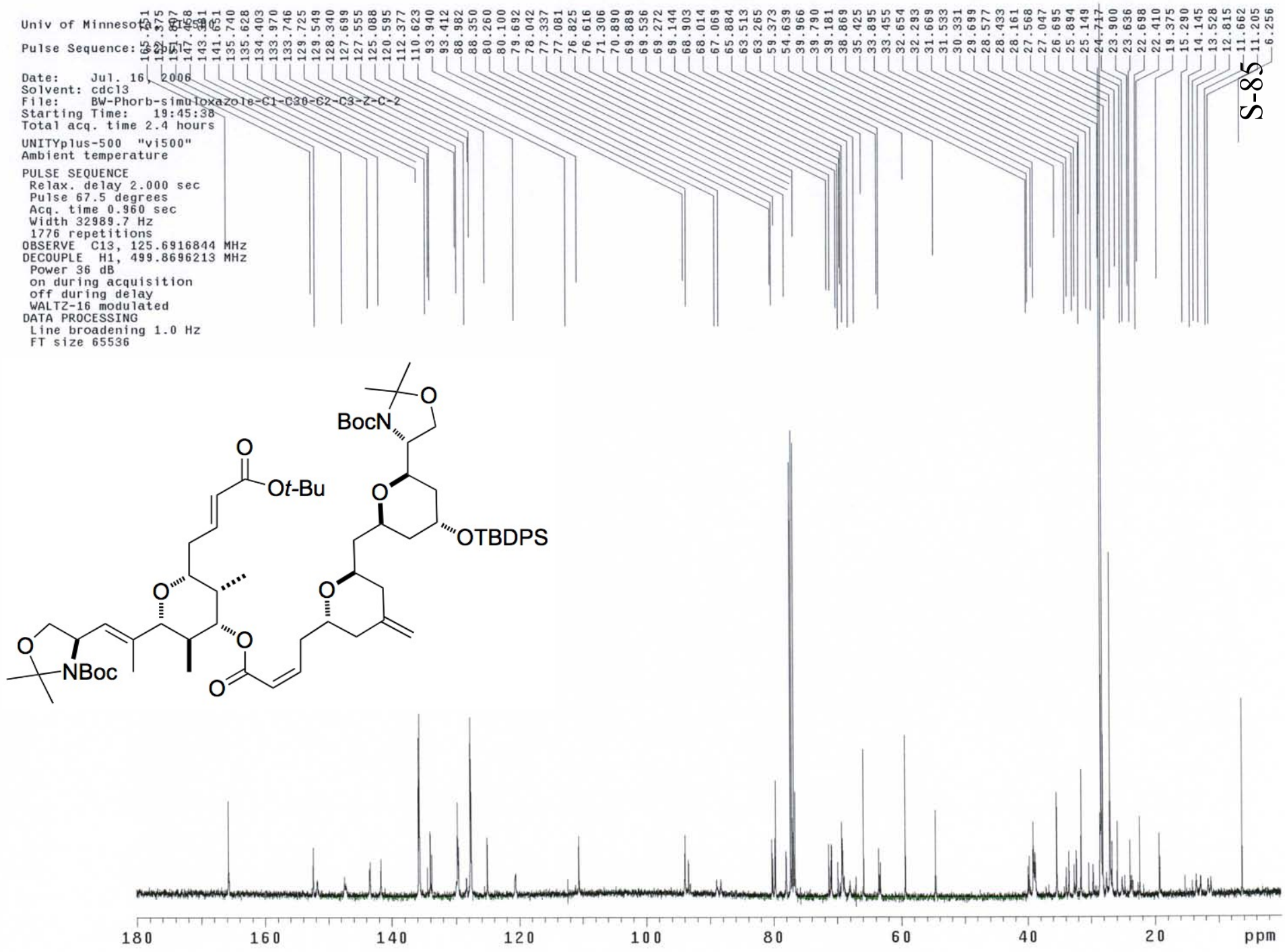
^{1}H NMR spectrum for compound **54**



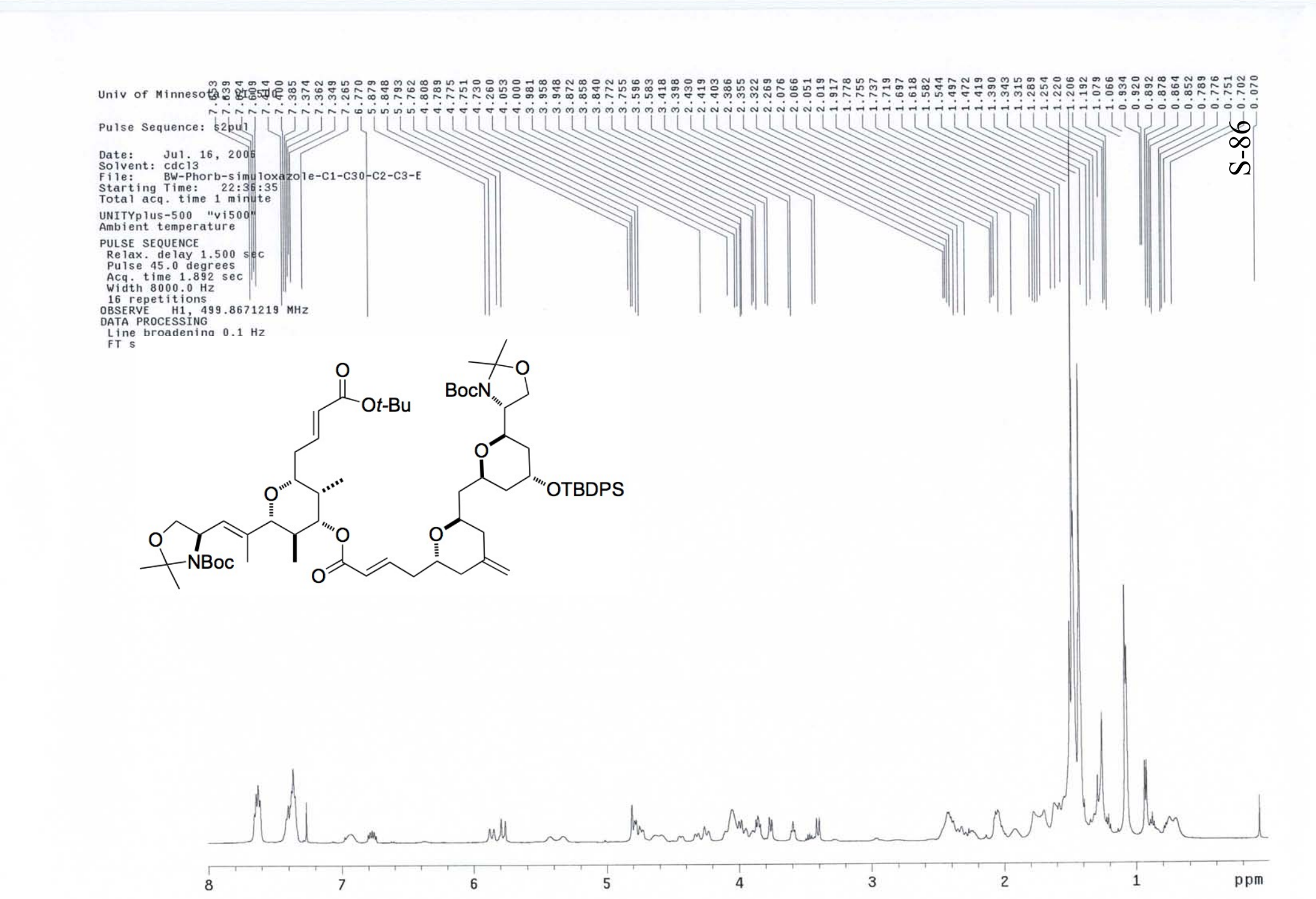
^{13}C NMR spectrum for compound **54**



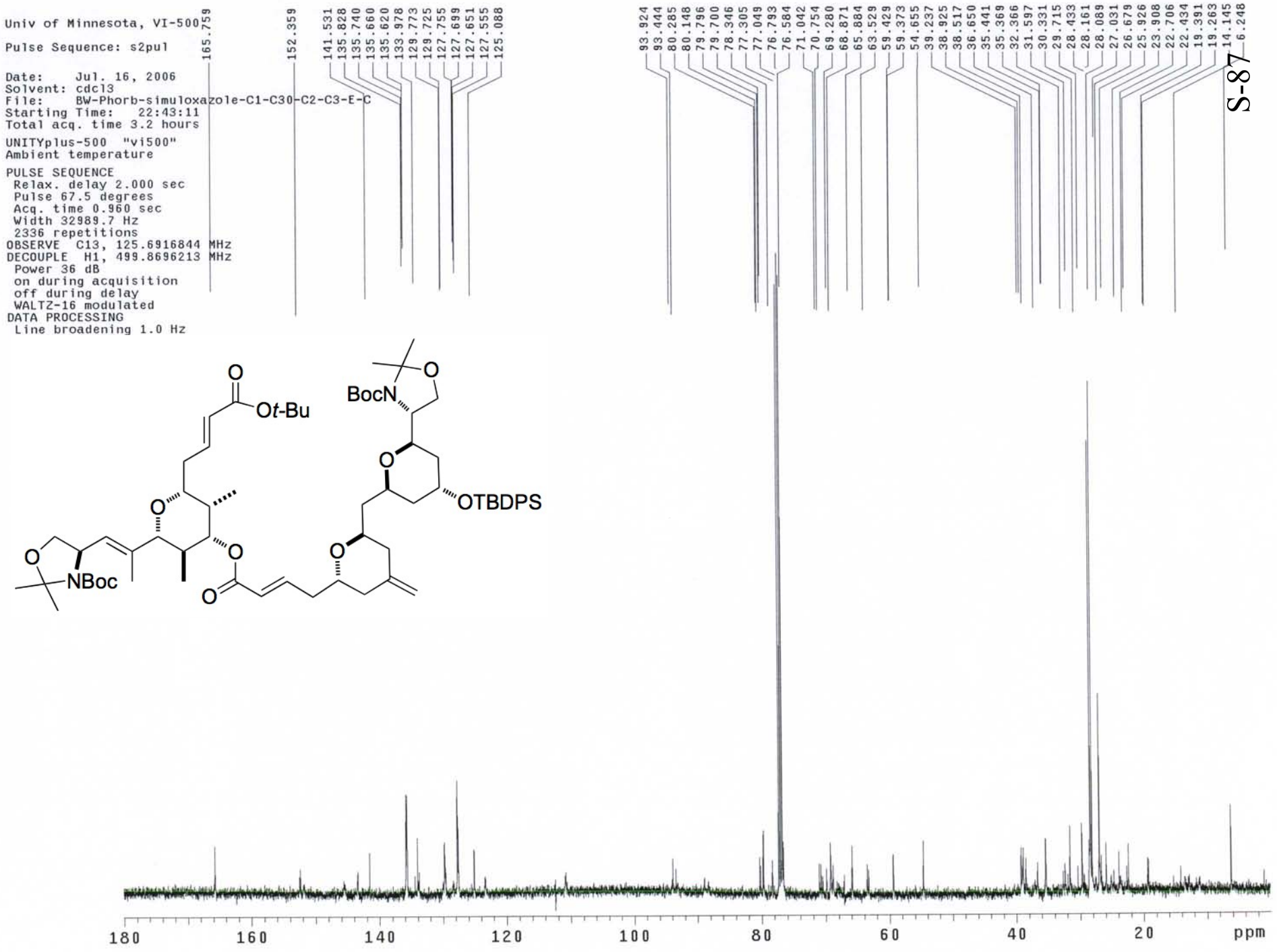
^{1}H NMR spectrum for compound (2*Z*)-**47**



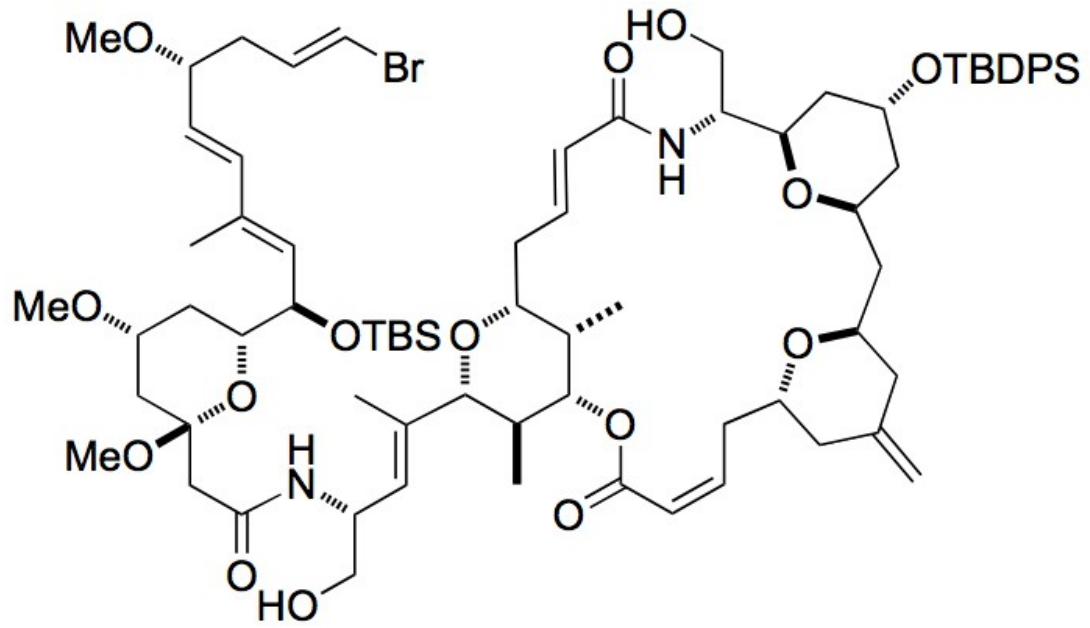
^{13}C NMR spectrum for compound (2*Z*)-**47**

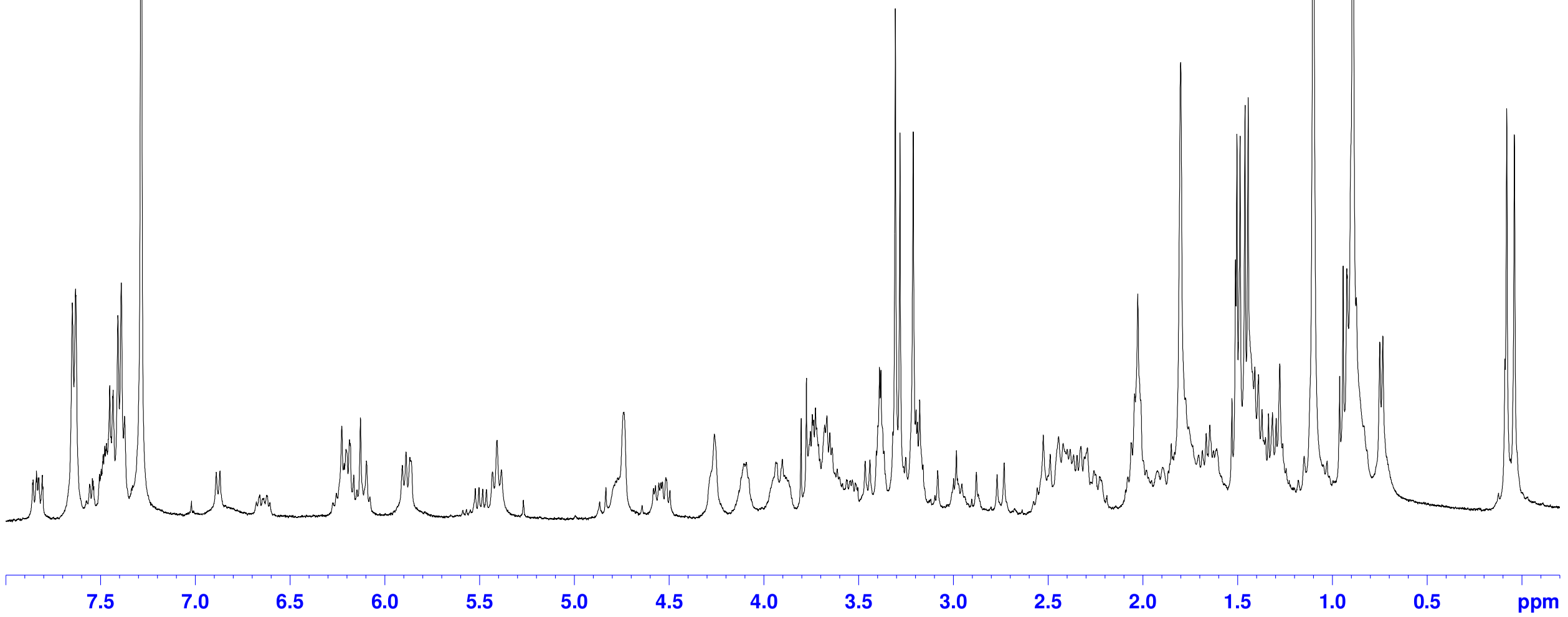


^{1}H NMR spectrum for compound (2*E*)-**47**



^{13}C NMR spectrum for compound (2*E*)-**47**






```
Current Data Parameters
NAME      phorbbisamide A
EXPNO                   1
PROCNO                  1

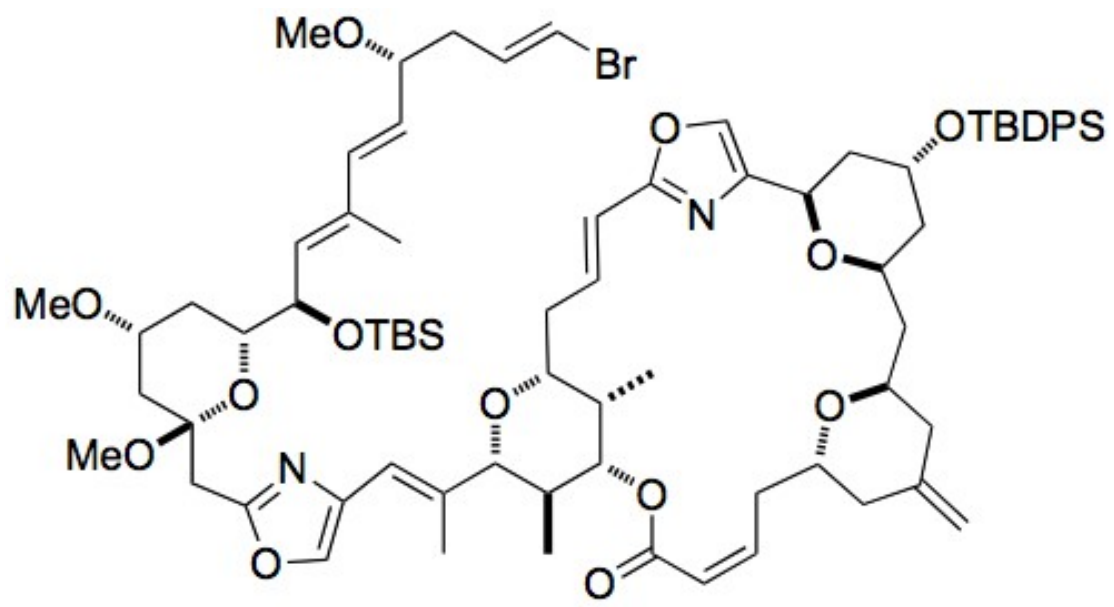
F2 - Acquisition Parameters
Date_            20070728
Time                1.18
INSTRUM            spect
PROBHD   5 mm QNP 1H/13
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             8278.146 Hz
FIDRES          0.126314 Hz
AQ             3.9584243 sec
RG                 203.2
DW                60.400 usec
DE                 6.00 usec
TE                300.2 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                   1H
P1                 13.00 usec
PL1                 0.00 dB
SFO1         400.1324710 MHz

F2 - Processing parameters
SI                 32768
SF           400.1300000 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00

1D NMR plot parameters
CX                 30.00 cm
CY                 19.00 cm
F1P               11.000 ppm
F1              4401.43 Hz
F2P               -1.000 ppm
F2              -400.13 Hz
PPMCM           0.40000 ppm/cm
HZCM          160.05200 Hz/cm
```

^{1}H NMR spectrum for crude compound **44**

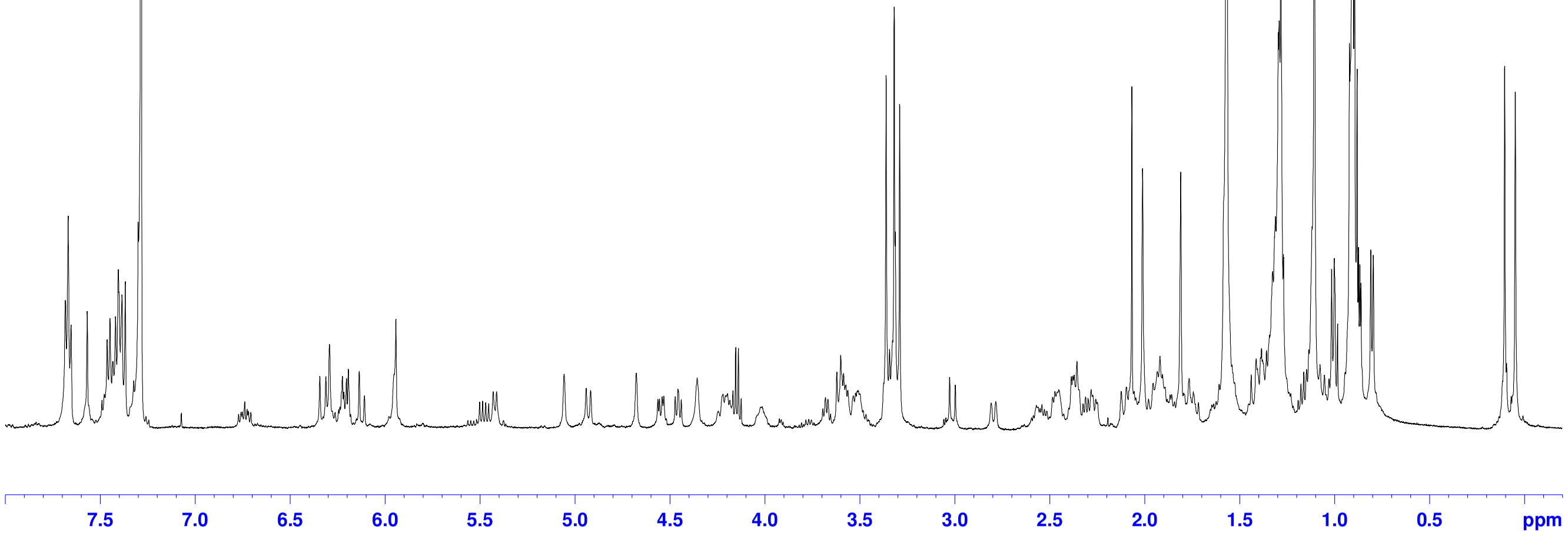



```
Current Data Parameters
NAME      C13OTBDPS-C38OTBS-C33OMe-Phorboxazole A
EXPNO                  1
PROCNO                 1

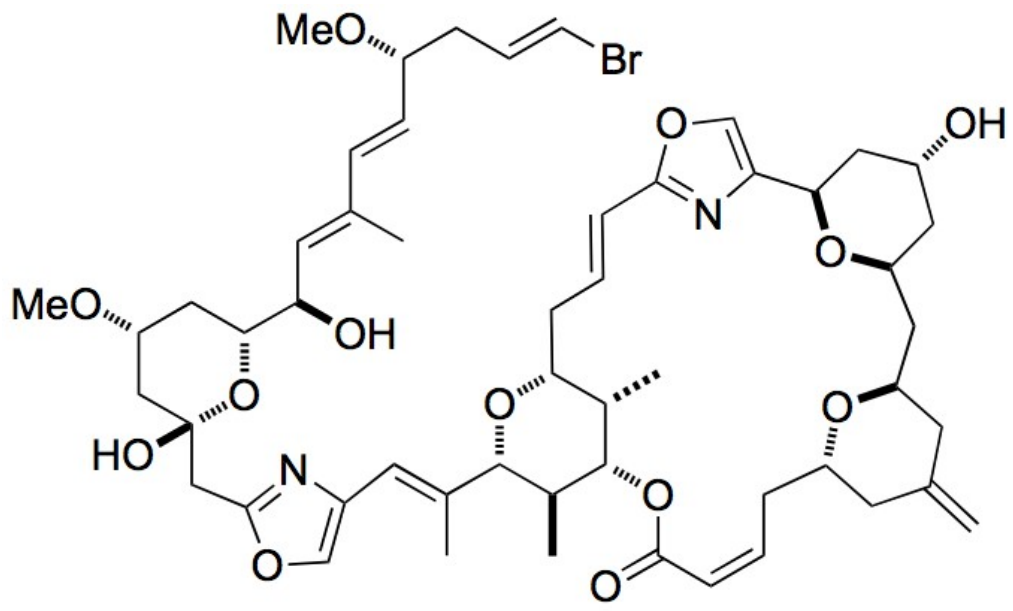
F2 - Acquisition Parameters
Date_           20070813
Time              22.09
INSTRUM           spect
PROBHD    5 mm Multinucl
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                  336
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ             3.1719923 sec
RG                645.1
DW                48.400 usec
DE                 6.00 usec
TE                300.2 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

======== CHANNEL f1 ========
NUC1                1H
P1                14.80 usec
PL1               -1.00 dB
SFO1         500.0230878 MHz

F2 - Processing parameters
SI                 32768
SF           500.0200000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

^{1}H NMR spectrum for compound **27**



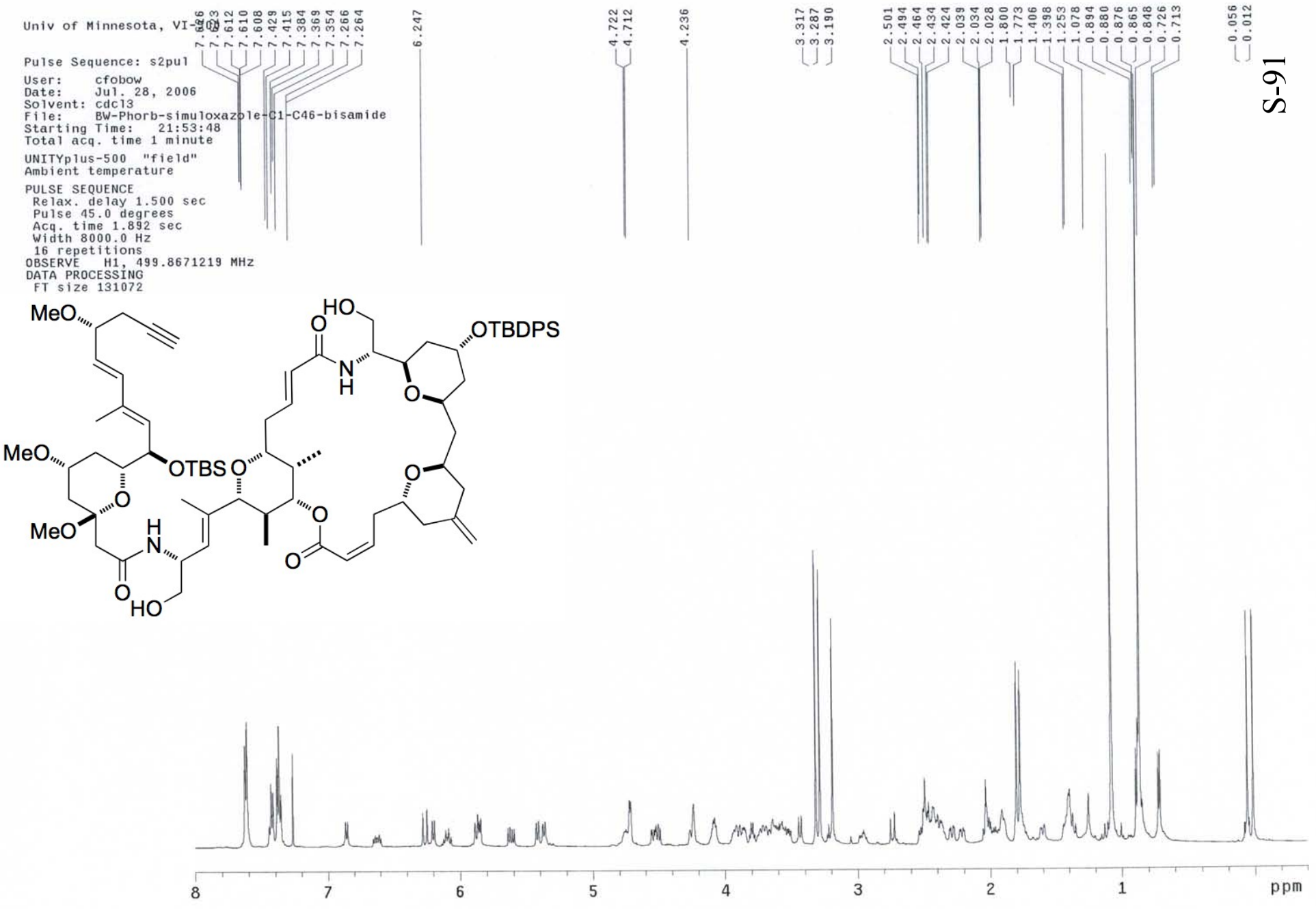

```
Current Data Parameters
NAME     phorboxazole A
EXPNO                 1
PROCNO                1

F2 - Acquisition Parameters
Date_          20070817
Time              17.15
INSTRUM           spect
PROBHD   5 mm Multinucl
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                  144
DS                    2
SWH           10330.578 Hz
FIDRES         0.157632 Hz
AQ            3.1719923 sec
RG                724.1
DW               48.400 usec
DE                6.00 usec
TE               300.2 K
D1           1.00000000 sec
MCREST       0.00000000 sec
MCWRK        0.01500000 sec

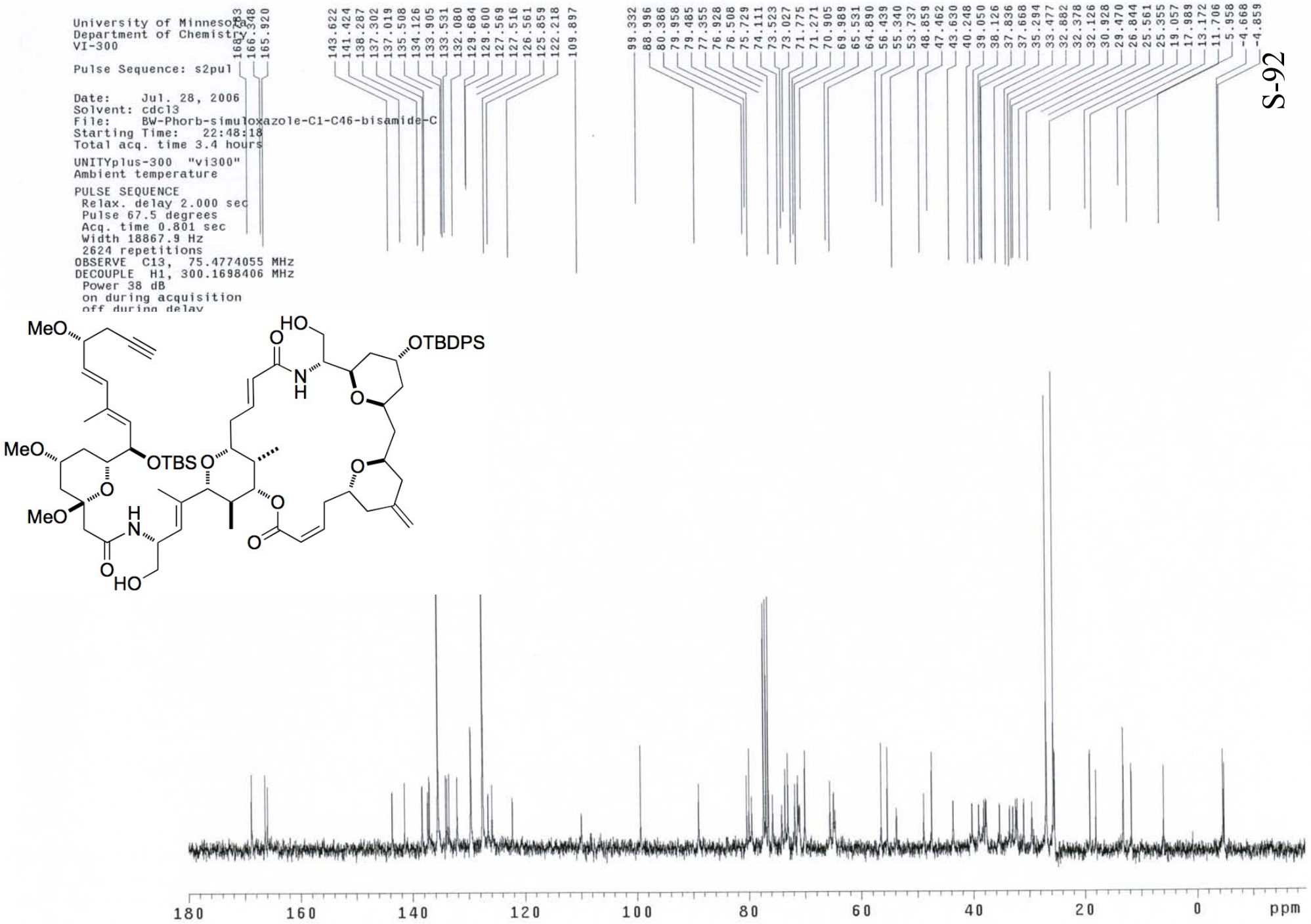
======== CHANNEL f1 ========
NUC1                  1H
P1                14.80 usec
PL1               -1.00 dB
SFO1         500.0230878 MHz

F2 - Processing parameters
SI                32768
SF          500.0200000 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```

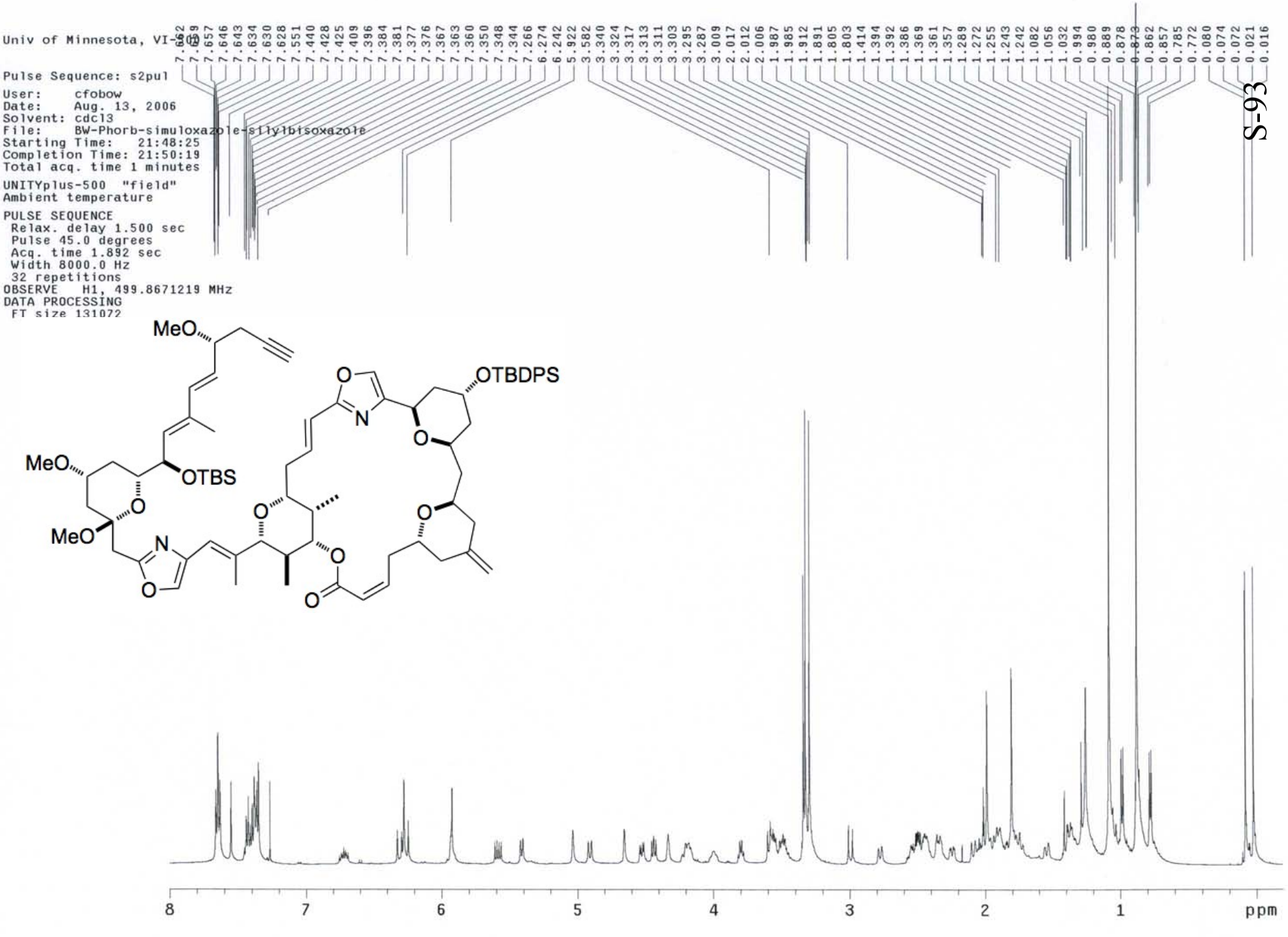
^{1}H NMR spectrum for phorboxazole A (**1**)



^{1}H NMR spectrum for compound **45**



^{13}C NMR spectrum for compound **45**



S-93

^{1}H NMR spectrum for compound **33**

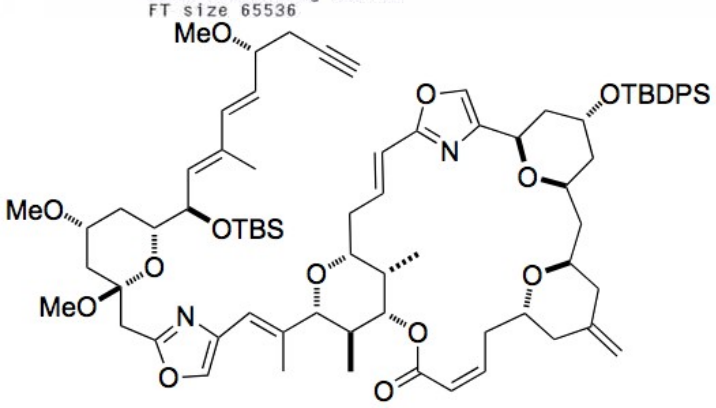
Univ of Minnesota VI 500

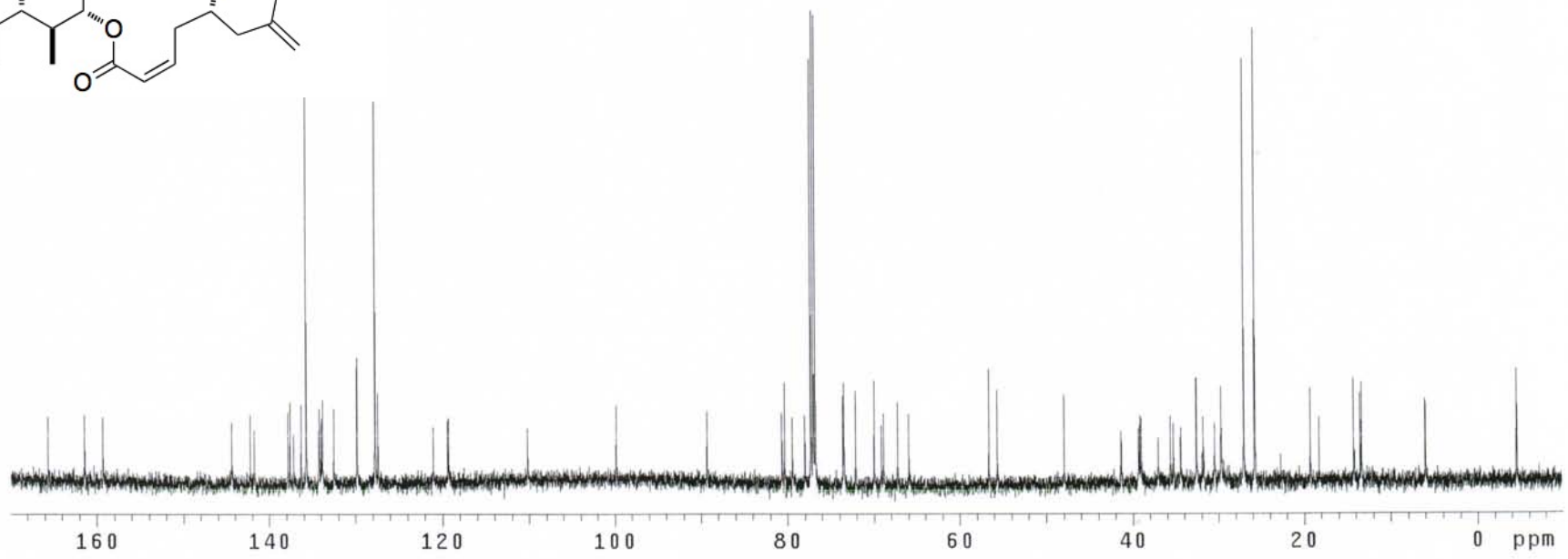
Pulse Sequence: s2pul

Date: Aug. 13, 2006
Solvent: cdcl3
File: BW-Phorb-simuloxazole-silylbisoxazole-C
Starting Time: 21:52:42
Total acq. time 2.2 hours

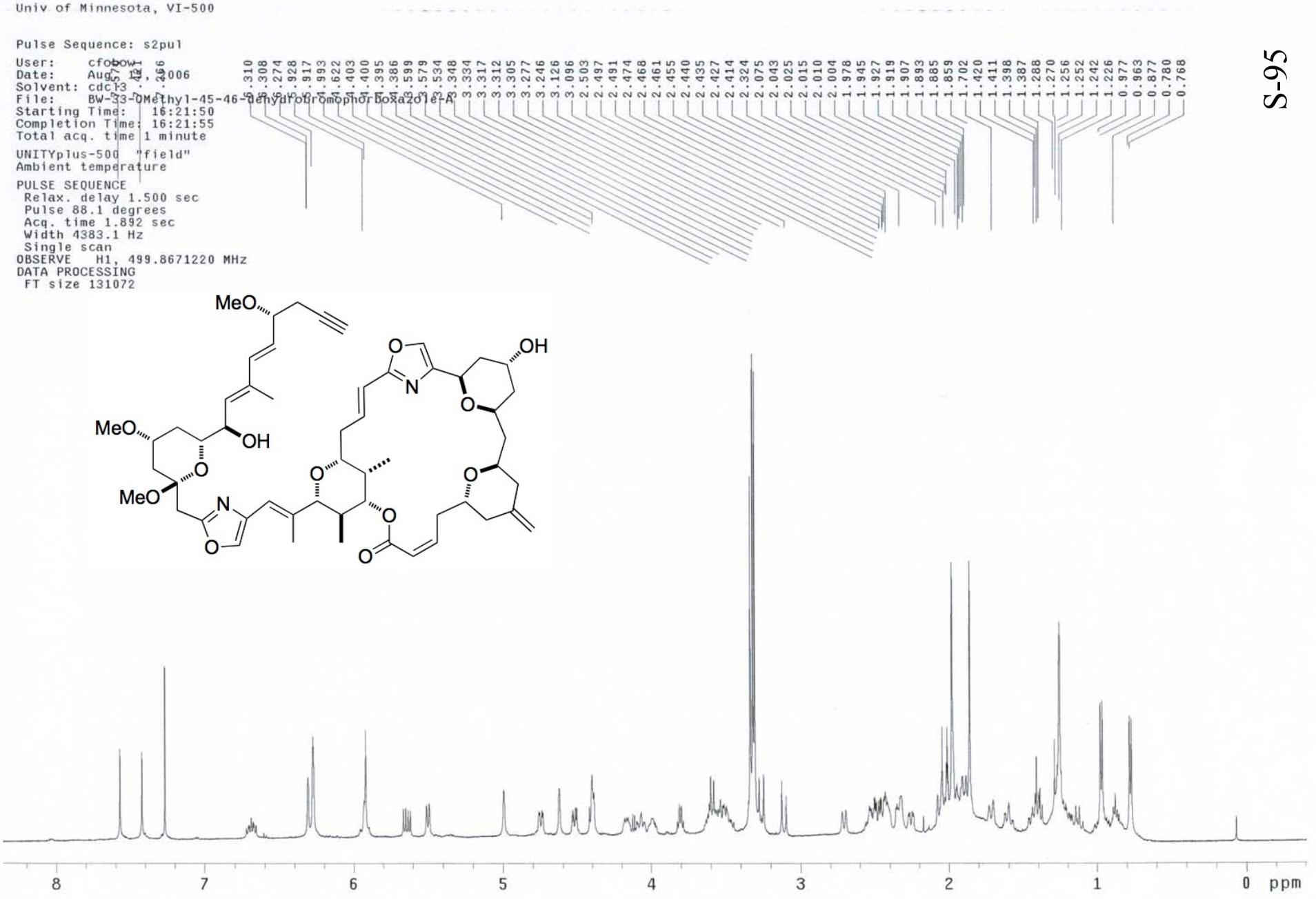
UNITYplus-500 "vi500"
Ambient temperature

PULSE SEQUENCE
Relax. delay 2.000 sec
Pulse 67.5 degrees
Acq. time 0.960 sec
Width 32989.7 Hz
1600 repetitions
OBSERVE C13, 125.6916844 MHz
DECOUPLE H1, 499.8696213 MHz
Power 36 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 65536

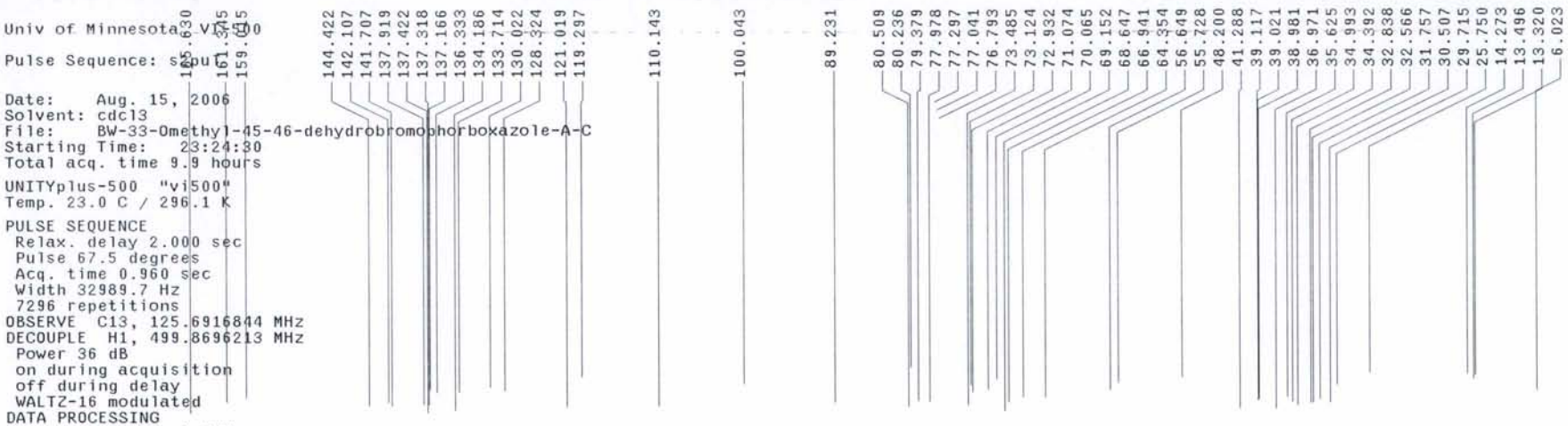


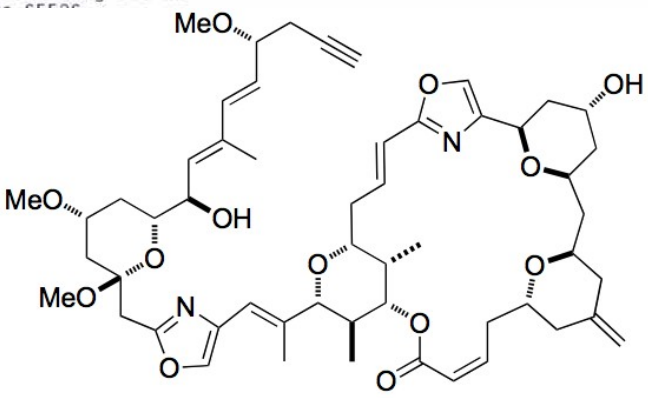


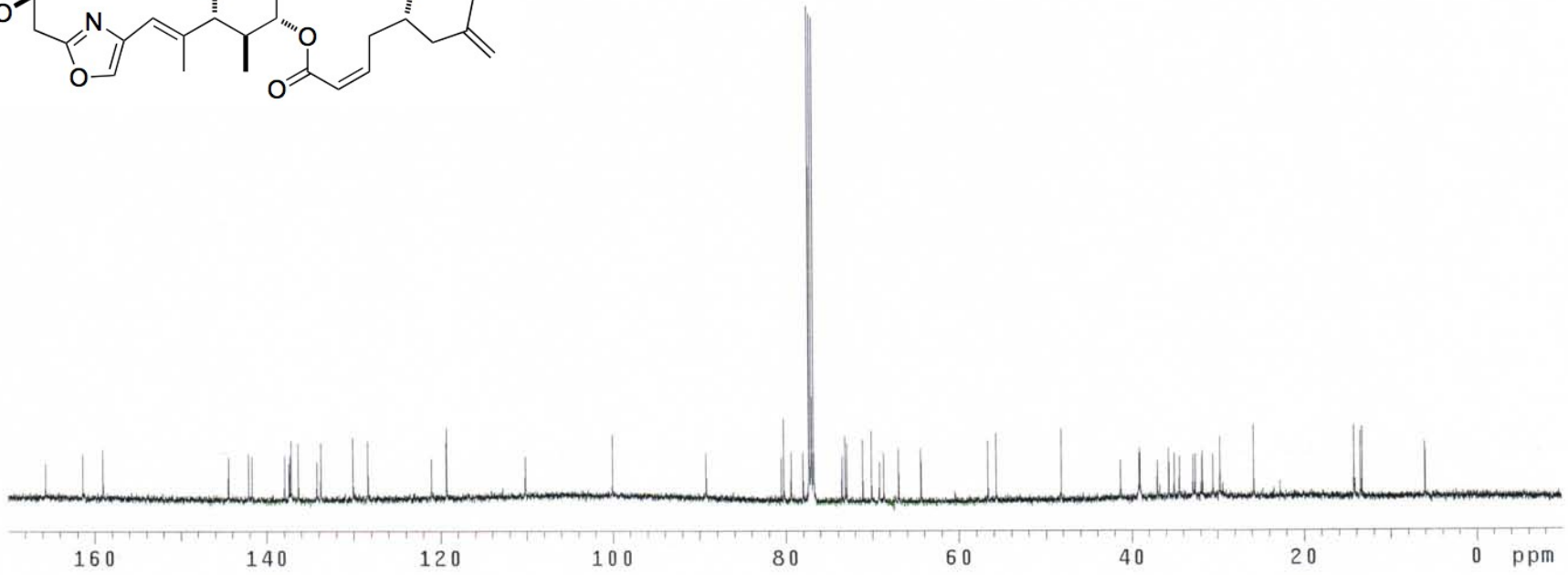
^{13}C NMR spectrum for compound **33**



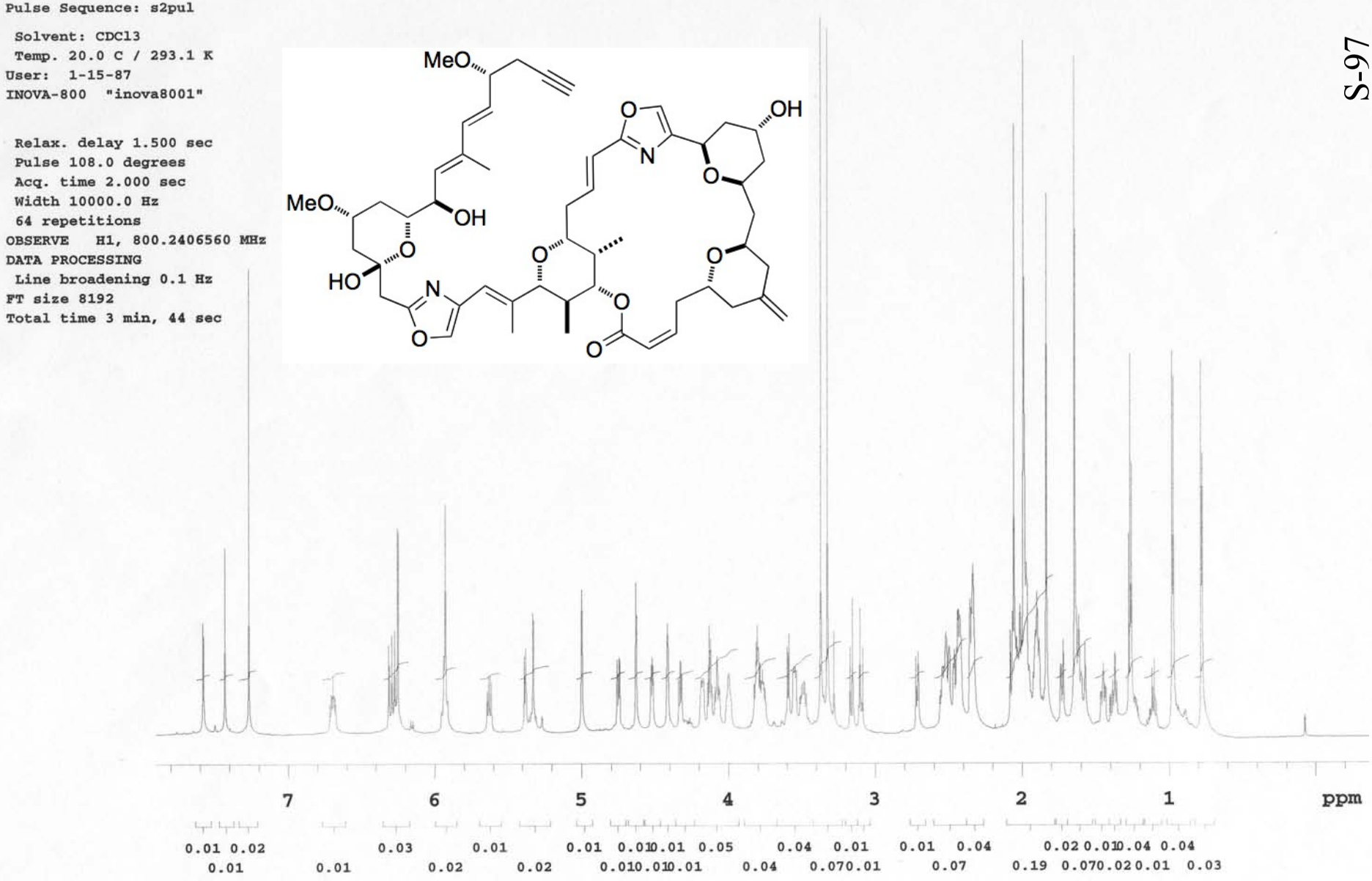
^{1}H NMR spectrum for compound **34**







^{13}C NMR spectrum for compound **34**



^{1}H NMR spectrum for 45,46-dehydrobromo-phorboxazole (**35**)

45-46DBBAC

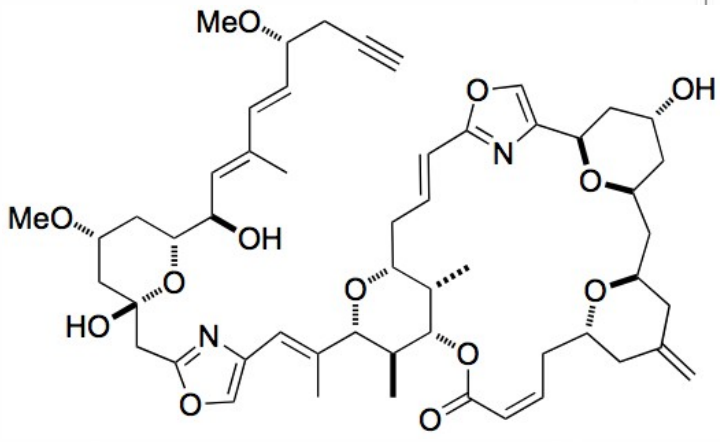
University of Minnesota
Department of Chemistry
VAC-300

Pulse Sequence: s2pul

Spin rate: 20
Date: Aug. 7, 2002
Solvent: CDCl3
Starting Time: 15:59:17
Total acq. time 18.1 hours

UNITYplus-300 "vxr300"
Ambient temperature

PULSE SEQUENCE
Relax. delay 0.100 sec
Pulse 67.5 degrees
Acq. time 0.801 sec
Width 18867.9 Hz
23248 repetitions
OBSERVE C13, 75.3995910 MHz
DECOUPLE H1, 299.8604072 MHz
Power 38 dB
on during acquisition
off during delay
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.5 Hz
FT size 65536



165.483 161.193 159.910 144.314 141.925 141.566 137.833 137.490 137.375 137.177 135.787 133.994 133.574 129.642 128.108 120.879 119.184 118.375 110.008 96.511 89.068 80.404 80.122 79.190 77.885 77.335 77.114 76.915 76.488 73.366 72.900 72.381 70.801 70.121 69.938 69.022 68.518 66.823 64.289 60.327 56.541 55.701 41.151 40.403 39.563 38.907 36.853 34.876 34.265 33.777 32.945 32.441 31.593 30.380 29.616 25.669 14.135 13.845 13.364 13.242 5.936

220 200 180 160 140 120 100 80 60 40 20 0 ppm

^{13}C NMR spectrum for 45,46-dehydrobromo-phorboxazole (**35**)